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THE COPPER DRAGON DE BEFFROI, GHENT.

A remarkable example of mediæval metal-working seen on the occasion of the visit of Members of the Institute to Ghent in August 1913. A description of the dragon appears on the reverse side of the title-page.

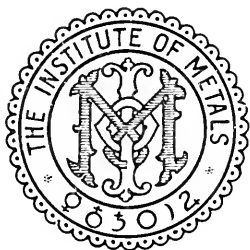# THE JOURNAL

OF THE

INSTITUTE OF METALS

VOLUME X

EDITED BY

G. SHAW SCOTT, M.Sc.

SECRETARY

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THE COPPER DRAGON DE BEFFROI, GHENT.

Description of Frontispiece.

The Dragon is placed at the top of the Beffroi, Ghent, at a height of 300 feet.

It is made entirely of copper sheet, riveted together, and gilded. In length it is 11 feet 6 inches, measured from the tip of the tongue to the end of the tail. The height is 6 feet, from the feet to the ears, and the width 2 feet 6 inches.

The Dragon was constructed in Ghent in 1377–78, and was regarded as the guardian of the city treasury and archives. It was for this reason that it was placed in its dominating position at the top of the tower.

During the Middle Ages it was taken down several times for regilding. On one of these occasions, in 1543, there was placed in it, prior to its re-erection, a copper box containing money of the period and parchment records, a box which was opened some hundreds of years later, and which is now in the Museum at Ghent.

The last time the Dragon was taken down was in 1912, when it was repaired and regilded in readiness for the Ghent International Exhibition of 1913.

THE INSTITUTE OF METALS

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THE INSTITUTE OF METALS

SECTION I.

MINUTES OF PROCEEDINGS.

GHENT MEETING.

The Fifth Annual Autumn Meeting of the Institute of Metals was held in the Palais des Fêtes of the International Exhibition, Ghent, Belgium, on Thursday and Friday, August 28 and 29, 1913, Professor A. K. Huntington, Assoc.R.S.M., President, in the chair.

Official Welcome by the University of Ghent.

The Rector of the University of Ghent, Professor H. Schoentjes, welcomed the members to Ghent on behalf of the University. He said : " C'est pour l'Université de Gand, et pour son recteur en particulier, un grand honneur que d'avoir l'occasion de vous souhaiter la bienvenue à l'ouverture de vos assises. L'Institute of Metals, quoique de création récente, a excité un intérêt considérable dans le monde scientifique ; j'en vois une preuve indénieable dans la grande affluence des adhérents à votre congrés et dans le renom des personnalités que je vois figurer parmi eux.

" Pour ne citer que les membres de votre bureau, les noms du professeur Huntington, de Sir Gerard Muntz, des professeurs Carpenter, Turner, de Mr. Boeddicker, du Dr. Rosenhain, sont hautement appréciés non seulement par les spécialistes de la métallurgie, mais encore par les physiciens.

" En particulier, les travaux de votre vénéré président, le professeur Huntington, travaux poursuivis pendant trente ans, ont suscité de brillantes applications de la science.

" Nous, hommes du Continent, nous apprécions hautement les travaux scientifiques anglais, si concrets, si précis, et

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empreints d'une si puissante originalité. Les travaux de
métallurgie de votre institut présentent, je n'en doute
aucunement, les mêmes qualités précieuses.

" L'Université de Gand, que rien de ce qui touche à la
science ne peut laisser indifférente, est particulièrement
heureuse et fière, de ce que vous ayez bien voulu tenir votre
meeting dans notre vieille cité, et apporter à nos savants et à
nos industriels, les lumières de vos études et de vos méthodes.

" Une institution et des réunions comme les votres n'ont
pas uniquement une portée scientifique ; elles ont une signifi-
cation· plus haute, plus noble encore ; elles attestent que le
monde intellectuel ne connaît ni frontières, ni races, ni langues,
que la science est le grand promoteur de la solidarité et de
la fraternité humaines."

The PRESIDENT, in reply to the speech of welcome, said :
" Je commencerai par exprimer à M. le Recteur notre pro-
fonde gratitude pour les paroles si obligeantes et si cordiales
qu'il a bien voulu nous addresser de la part de la Direction
de l'Université.

" En verité la science ne connait ni nationalités ni limites
geographiques. Nos réglements sont établis de manière à
admettre comme membres tous ceux qui s'interressent aux
connaissances que nous cherchons à cultiver, quelle que soit
leur nationalité.   Parmi les preuves de succès que nous avons
obtenus comme Institut, les demandes d'admission que nous
sont parvenues de toutes les parties du monde ne sont pas
les moins importantes.   La liste comprenant non seulement
personnes qui se sont distinguées en qualité de fabricants
prospères, entre autres votre aimable et éminent compatriote
M. Carels, mais encore les noms de quelques-uns des plus
haut placés par leur science.   Je pourrais étendre beaucoup
cette énumeration mais cela m'entraînerait trop loin.

" Je suis sur que j'interprète correctement vos sentiments
de sympathie envers le but que nous poursuivons, qui est,
en un mot, l'application de la science métallurgique aux
arts pratiques, en tout ce qui se rapporte aux métaux autres
que le fer et l'acier.

" Le renom de la Maison Cockerill fondée par un Anglais

et dirigée pendant plusieurs generations par le génie belge retentit dans le monde entier. L'Usine Veille Montagne occupe facilement première place quand on parle du zinc, vos inventions de fours-à-coke sont très estimées chez nous. Ce ne sont que des exemples de votre haute position dans l'industrie métallurgique.

"Je m'arrète pour ne pas abuser plus longtemps de vos moments. Je saissis avec empressement cette occasion— notre première réunion sur le Continent—pour vous témoigner nos sentiments de consideration et notre vive gratitude pour l'accueil si cordial, si bienveillant reçu par les membres de l'Institute of Metals."

The PRESIDENT then proceeded to occupy the chair, the Rector having withdrawn.

The Minutes of the previous meeting, held in London on March 11 and 12, 1913, having been taken as read, were confirmed.

COUNCIL FOR 1914.

The SECRETARY (Mr. G. Shaw Scott, M.Sc.) read a list of members nominated by the Council, and to be balloted for in connection with the election of the Council for 1914, which list was as follows :—

President.

*Engineer Vice-Admiral Sir H. J. ORAM, K.C.B., F.R.S.

Vice-Presidents.

(Three to be elected.)

†Professor H. C. H. CARPENTER, M.A., Ph.D.	Manchester.
†Mr. SUMMERS HUNTER	Wallsend-on-Tyne.
*Mr. R. KAYE GRAY	London.

Members of Council.

(Five to be elected.)

†Mr. L. ARCHBUTT	Derby.
†Mr. G. HUGHES	Horwich.
†Dr. W. ROSENHAIN, F.R.S. . .	Teddington.
†Dr. R. S. HUTTON	Sheffield.
†Mr. W. MURRAY MORRISON . .	London.

* New Nomination.

† Retires in accordance with Articles, Section iii, 15, and re-nominated.

The PRESIDENT stated that the result of the ballot would be declared at the Annual General Meeting, to be held in London on March 17, 1914. The President also reminded the meeting that, in accordance with the Articles, Section iii, 16, any ten members might also, at the present meeting, nominate a candidate other than one of those nominated by the Council, but none of the members present exercised their right in this matter.

ELECTION OF MEMBERS.

The SECRETARY read the following list of names of candidates who had been elected members of the Institute :—

NAME.	ADDRESS.	QUALIFICATIONS.	PROPOSERS.
Boscheron, Louis.	Hollogne-aux-Pierres, Belgium	Engineer-Manager, la Vieille Montagne Works	Sir H. J. Oram. W. Rosenhain. W. H. Johnson.
Caldwell, Robert John, D.Sc.	105 Wellesley Avenue, Belfast	Chemist	C. H. Desch. A. V. Hussey. R. Crighton.
Chapman, Arthur Jenner	6 & 7 Coleman Street, E.C.	Analytical Chemist	G. T. Holloway. T. Girtin. F. W. Harbord.
Colver-Glauert, Edward, Dr. Ing.	Brocklands, Osgathorpe, Sheffield	Demonstrator in Metallurgy, Sheffield University	G. B. Brook. C. H. Wilson. R. S. Hutton.
Dixon, Eng. Com. Robert Bland, R.N.	H.M. Dockyard, Portsmouth	Manager, Eng. Dept., H. M. Dockyard, Portsmouth	Sir H. J. Oram. G. G. Goodwin. J. McLaurin.
Espir, Fernand	3 East India Avenue, E.C.	Merchant & Agent for Tréfileries & Laminoirs du Havre	F. Smith. F. A. B. Lord. T. Bolton.
Forster, Joseph William	P.O. Box 56, East Rand, J'burg, S. Africa	Chief Mechanical Engineer, East Rand Mines	J. Connolly. A. K. Huntington. T. A. Bayliss.
Muirhead, William	Holmfield, Kirkintilloch, Renfrewshire	Works' Chemist	J. A. C. Edmiston. J. S. G. Primrose. G. T. Beilby.
Read, Prof. Arthur Avery, M.Met.	University College, Cardiff	Professor of Metallurgy	A. K. Huntington. T. Turner. O. F. Hudson.
Renaud, Victor	22 Quai des Moines, Ghent, Belgium	Civil Engineer, Lecturer in Ghent University	W. Rosenhain. W. H. Johnson. T. A. Bayliss.
Skillman, Verne	Lumen Bearing Co., Buffalo, N. Y., U.S.A.	Metallurgist	W. M. Corse. W. H. Bassett. G. Clamer.
Turner, Harold	73–79 Eyre Street, Sheffield	Gold and Silver Refiner	W. R. Barclay. E. A. Smith. G. B. Brook.
Wüst, Prof. Fritz, Dr. Phil., Dr. Ing.	Ludwigsalle 47, Aachen, Germany	Professor of Metallurgy	W. Rosenhain. Sir H. J. Oram. T. A. Bayliss.

CONGRATULATIONS TO PROFESSOR CARPENTER.

The PRESIDENT said that, before proceeding with the papers, they would like to congratulate Professor Carpenter on his appointment to the Chair of Metallurgy in the Royal School of Mines. Professor Carpenter had been with them from the commencement of the Institute, and, in fact, the Institute owed its foundation largely to Professor Carpenter's efforts. He was afraid that in his new position the Professor would not remain quite so closely in touch with the Institute as hitherto ; but he hoped after he had got well started he would be able to give the Institute some of his time. As they knew, the Chair of the Royal School of Mines had to do very largely with the extractions of metals from their ores, rather than with their various applications, and Professor Carpenter would have to devote his attention to that side probably more than he had done hitherto. But what would be their loss would be the gain of the Institution of Mining and Metallurgy, and of metallurgy in general. No doubt there was plenty of room, and would continue to be for a long time, for the physical and mechanical side of metallurgy, to deal with the practical extraction of ores. Great advances in recent years had been made in the treatment of various ores by the development of processes which were purely of a physical nature. For example, they had the magnetic separation of ores, which was purely a physical question, and there were other processes —*e.g.* the flotation process. Probably, in the course of years that side of metallurgy would be applied more and more to the extraction of metals from their ores. They offered their sincere congratulations to Professor Carpenter.

Professor T. TURNER, M.Sc., Vice-President and Honorary Treasurer, said that he would like to join very heartily in the congratulations to Professor Carpenter on his appointment, and those congratulations would be more hearty because, like Professor Huntington, he (Professor Turner) was an old School of Mines man himself ; and it had been a pleasure to him to serve on the Bessemer Memorial Committee for the equipment of the laboratory of that Institution. He felt sure, that in

Professor Carpenter, the Metallurgical Department of the Royal School of Mines would have a head who would extend its work, and carry on its traditions, while he was equally sure they would not lose his hearty co-operation in the work of the Institute of Metals. They wished Professor Carpenter every success.

Professor H. C. H. CARPENTER, M.A., Ph.D., Vice-President, said that was a quite unexpected tribute to himself. While it was true that the branch of metallurgy at South Kensington with which he would have to do would in the main be rather different from that of his past work, the authorities took a very broad view of the subject of metallurgy, and he was given to understand that he would have absolute freedom with regard to research work. Therefore, he hoped that he might in future be permitted to cross swords with their President, as he had done in the past, on points of scientific interest. He felt that the undertaking was a very great responsibility, and he would like to say that his experience with the Institute of Metals, and particularly the benefit he had derived from their discussions, would be of the greatest use to him in the future. He thanked them very heartily for their kind congratulations.

CORROSION COMMITTEE.

The PRESIDENT said that they would shortly be hearing Dr. Bengough present his Second Report on the subject of the corrosion of condenser tubes. The future of this work depended to a great extent upon what funds were available, a matter which was naturally one of considerable anxiety to the Corrosion Committee. It was hoped by the Committee that the publication of the Report would result in their obtaining promises, and not merely promises, of additional financial assistance. The funds had become practically exhausted, but they had recently sent out some advance copies of the Report, and already those Reports, which had only been available for a few days, had brought many generous promises, which were announced that day for the first time. They

included a donation of £200, and a further annual subscription of £100 from the Brass and Copper Tube Association, 25 guineas from Lloyds' Register, £25 from Vickers Limited, £10 from the Midland Railway Company, and several other donations. The full list would be published shortly. The Committee were still in need of further promises, and additional gifts for the promotion of the work would be heartily welcomed by the Secretary of the Institute on behalf of the Committee.

READING OF PAPERS.

Papers were then read by the following : Dr. G. D. Bengough, M.A. (Liverpool), and Mr. R. M. Jones, M.Sc. (Liverpool); Dr. W. Rosenhain, F.R.S. (Teddington), and Mr. D. Ewen, M.Sc. (Teddington); and Dr. T. K. Rose (London). Each paper was followed by a discussion, a hearty vote of thanks being accorded in each case, on the motion of the President, to the respective authors. The meeting adjourned at 1 P.M. until 10 o'clock on Friday morning, August 29, 1913.

SECOND DAY'S PROCEEDINGS.

FRIDAY, *August* 29, 1913.

The Second Session of the General Meeting was held in the Palais des Fêtes of the International Exhibition, Ghent, on the morning of Friday, August 29, Professor A. K. Huntington, Assoc.R.S.M., President, again occupying the chair.

READING OF PAPERS.

Papers were read by the following : Dr. W. M. Guertler (Berlin); Mr. J. H. Chamberlain, M.Sc. (Birmingham); Professor S. L. Hoyt (University of Minnesota, Minn. U.S.A.) and Mr. F. Johnson, M.Sc. (Birmingham); and papers by : Dr. Cecil H. Desch and Mr. S. White, B.Sc. (Glasgow); Mr. H. Garland (Cairo); Professor A. A. Read, M.Met. (Cardiff); and Mr. T. West, M.Sc. (Montreal), were taken as read. Each

of the papers actually read was followed by a discussion, and a
hearty vote of thanks was accorded in the case of every paper,
on the motion of the President, to the respective authors.

Official Welcome by His Majesty's Consul-General for Belgium.

During the discussion of Professor Hoyt's paper a visit was
paid to the meeting by Sir E. Cecil Hertslet, Kt., His
Majesty's Consul-General for Belgium who had come to offer
the members of the Institute an official welcome to Ghent.

Sir Cecil Hertslet said that occupying, as he did, the
position of His Majesty's Consul-General for Belgium he
thought it his duty, and it was indeed a very great pleasure, to
offer them on the part of His Majesty's Government a very
warm welcome to that country. The present, he understood from
their President, was the first occasion on which the Institute
of Metals had held its conference abroad, and he felt certain
they would carry back with them to their own country, and
the foreign members to their respective countries, a happy
and agreeable souvenir of the days they had spent in Ghent.
Mr. Wintour, the British Commissioner-General for the Ghent
Exhibition, had unfortunately been recalled to London by his
official duties. He was also the head of the Exhibition's
Branch of the Board of Trade, and he (Sir Cecil) had been
asked by him to express to them his regret that he was not
there personally to receive them and make them at home in
the British section. But in his absence the Commissioner's
staff were prepared to receive them, and offer them every
possible facility for a thorough inspection of the very interest-
ing section which His Majesty's Government had installed at
the Ghent Exhibition. There were one or two points in con-
nection with that section to which he would like to draw
their attention. First of all, they had a very fine exhibit of
machinery, and especially of textile machinery. The reason
for that was that Ghent was the great centre of the textile
industries in Belgium ; in fact it was the Manchester of that
country. A very large proportion of the machinery used in

the cotton mills at Ghent came from Great Britain. They had also as a commercial exhibit a magnificent collection of British pottery. Until the Brussels Exhibition of 1910 British pottery was practically unknown on the Continent of Europe, but the British people sent their wares to the Brussels Exhibition, and they immediately succeeded in obtaining one of the first positions on the Continent for pottery. That was an exceedingly interesting exhibit, as showing what Great Britain could do in the manufacture of this class of goods. Besides that, His Majesty's Government had taken particular interest in the British section. There was an exhibit by the Home Office of our prison system, and exhibits by the Board of Agriculture of British fisheries. They would see also a very unique exhibit respecting tropical diseases, which had been forwarded by the Colonial and India offices. Then they would find an exhibit of post and telegraphs from the British Post Office, and they would see, above all, a most delightful section of arts and crafts, which had been also arranged by His Majesty's Government. He would not detain them further in the midst of their interesting discussions, except to say that, speaking on behalf of the Exhibitions Branch of the Board of Trade, they hoped that the visitors would spend as long a time as they could spare in the British section, and he could assure them that everyone connected with that section would be delighted to see them there.

The PRESIDENT, on behalf of the members, thanked Sir Cecil Hertslet for his kindness in coming to that meeting, and for the interest that he had displayed in their Proceedings.

CONCLUDING BUSINESS.

The PRESIDENT said that the major part of their business was now concluded, but there remained certain formalities which would be undertaken with very great pleasure. He proposed :—

"That the best thanks of the Institute be, and hereby are, tendered to the following gentlemen and firms whose kindness has contributed greatly to the success of the Ghent Meeting of the Institute :—

" (1) The Rector of the University of Ghent, Professor H. Schoentjes, for his kindly welcome on behalf of the University.

" (2) Sir E. Cecil Hertslet, Kt., H.M. Consul-General for Belgium, for his official welcome.

" (3) The directors of Messrs. Van de Kerchove and Messrs. Carels Frères for having kindly given permission to members of the Institute to visit their Works.

" (4) The Bourgmestre of the City of Ghent for his kind hospitality.

" (5) Monsieur V. Renaud, the Ghent Honorary Secretary of the Meeting, to whom the Institute is indebted for the well-considered arrangements made for the visit to Ghent ; also to Monsieur Gaston Carels for his valuable advice and practical assistance."

The PRESIDENT said that those who visited the Works on the previous day were greatly interested in what they saw of Messrs. Van de Kerchove's turbine engines. Messrs. Carels were one of the first to produce Diesel motors, which there were very few opportunities of seeing elsewhere.   Messrs. Carels were quite pre-eminent in that class of manufacture.   With regard to M. Renaud, who was the honorary local secretary to the meeting, he had kept himself very much in the background : but those who knew the secretary, and knew the great labour he had expended in connection with the meeting, would greatly appreciate the time he had placed at their disposal, and the excellent service he had rendered.   He must mention also their indebtedness to M. Gaston Carels for his valuable advice and practical assistance.   He had done a great deal for the Institute as a member, and the success of the meeting at Ghent was very largely due to him.   He would ask them to accord a hearty vote of thanks to all the gentlemen he had enumerated.

Professor CARPENTER said it was with very great pleasure he seconded the vote of thanks to those who had helped in promoting the success of the meeting.   He might call attention to a matter that had not been touched upon.   That was the first occasion on which their discussions had been conducted within the hearing of beautiful orchestral music,

and he could not help thinking that had had a very quietening and mollifying effect on the scientific discussions.

The votes of thanks were then put and carried with acclamation.

Sir GERARD MUNTZ, Bart., Past-President, said that before they parted he was sure they would all wish to join with him in a hearty vote of thanks to their worthy President for taking the chair in the way he had done. He had grasped the situation most admirably, and speaking as a past President, he fully sympathized with the President in his difficulties with gentlemen who spoke too long, and others who did not speak long enough. He had kept them all in order most pleasantly, and, in addition, there was hardly a paper that had come up for discussion on which he had not had a few words to say, either weighty or interesting, or both. They were all most grateful to him for the able and kindly manner in which he had filled his office.

Mr. G. A. BOEDDICKER, Vice-President, said that he had great pleasure in seconding the resolution.

The motion was put by Sir GERARD MUNTZ, and carried with acclamation.

The PRESIDENT, in reply, said that he heartily thanked them for the compliment. If the meeting had gone satisfactorily, he was amply rewarded. He thought that they had had a very satisfactory meeting, and were fortunate in having been able to keep their programme to time.

The proceedings then terminated.

RECEPTION AND VISITS.

In the evening of August 29, 1913, a Reception was given at the Town Hall, Ghent, by the Bourgmestre, M. Braun, who made a speech of welcome, to which the President, Professor Huntington, replied. The Members then made a tour of inspection of the historically interesting building under the Bourgmestre's guidance.

Visits took place on both days of the meeting after the morning session. In the afternoon of August 28 the Members visited the works of Messrs. Carels Frères (Diesel engines), and also those of Messrs. Van de Kerchove (Turbines). The following afternoon was spent in the Ghent International Exhibition, the party being under the guidance of M. Victor Renaud, of Ghent, the Honorary Local Secretary of the Meeting.

Thanks to the courtesy of Dr. W. Rosenhain, F.R.S., it is possible to insert herewith a photograph of a group of members taken at Ghent just before the party started for the above-mentioned visit to the Exhibition.

Group of Members at Ghent.

SECOND REPORT

TO THE

CORROSION COMMITTEE

OF THE

INSTITUTE OF METALS.*

By GUY D. BENGOUGH, M.A., D.Sc.

AND

RICHARD M. JONES, M.Sc.
(Respectively Lecturer in Metallurgy and Isaac Roberts Scholar
in the University of Liverpool)

INTRODUCTION.

In a former report to the Corrosion Committee of this Institute, one of the authors has drawn attention to the apparently erratic occurrence of corrosion in condensers, and the matter has been emphasized by numerous speakers both before and after the publication of that report. A number of explanations have been advanced to account for the pheno- menon, but few of them are based upon rigid experimental test. The recognized method of collecting information on corrosion hitherto has been to obtain it from engineers in charge of condensers engaged in practical work, and the general view of the importance of this method has been voiced by Arnold Philip,† who says :—

"It is the engineers who are actually responsible for the efficiency of condensers who are able to provide the necessary information upon which an opinion can be formed as to the causes of observed cases of corrosion, and in order to secure that such information is not overlooked at the time, it is very desirable that a suitable schedule of queries should be filled in."

In accordance with this view a list of questions relating to condenser tube corrosion was drawn up and circulated to mem- bers of the Institute, superintendent engineers, and others who

* Read at Autumn General Meeting, Ghent, August 28, 1913.
† *Journal of the Institute of Metals*, No. 1, 1912, vol. vii. p. 51.

have the care of condensers under their charge.   The list, in the form in which it was finally sent out, was drawn up at a meeting of the Corrosion Committee held during the Newcastle meeting of the Institute.

Accompanying the schedule a request was circulated for specimens of condenser tubes that had given good, bad, and average service under ordinary conditions of work.

A considerable number of forms were returned to the Institute, but comparatively few were completely filled up. Of these twenty have been selected, and the more important information contained in them has been tabulated on pages 16 and 17.   All the tubes referred to were of 70 : 30 brass or 70 : 29 : 1 alloy.   (Admiralty composition.)

The chief points of interest to be deduced from this table are :—

1. The extraordinary variation in the normal life of a tube, viz. from four to twenty-five years.   Supplementary inquiries conducted by the authors have proved conclusively that tubes from the same batch made by one manufacturer, when placed in different parts of a condenser, might resist corrosion for times which vary up to the proportion of 1 to 3.

2. The peculiar nature of the deterioration that resulted in the failure of the tube.   In nearly every case the deterioration was due to dezincification, resulting in a rotten and pitted tube.   In two or three cases tubes failed owing to local thinning, due, apparently, to the wearing away of the whole body of the tube near the water-inlet end.   This pheno-menon was comparatively rare.

3. The impossibility of correlating the failure of the tubes with the presence, or nature, of the electric lighting instal-lation.

4. The difficulty of connecting corrosion with any definite locality in the tube or condenser, though it would appear as if thinning were connected with the ends of the tubes at which the cooling water entered.

5. The shorter life of tubes in land installations, where dock, canal, or brackish water is used instead of sea water. Nevertheless, the Corrosion Committee, for good reasons, desired investigations in the first instance to be carried out

with natural sea water, and this has been used in all experiments described in the present paper, except where the contrary is stated.

A detailed examination of the scale attached to tubes, both good and bad, was made. In normal cases the scale could be regarded as made up of a number of layers of different composition. The outer layer consisted principally of ferric oxide, carbonates and chlorides of calcium and magnesium, calcium sulphate and sand ; the next layer consisted of basic chlorides and carbonates of copper and zinc, and was greenish in colour. The layer next the tube was brown or black, and consisted largely of cuprous and cupric oxide. There was, of course, no sharp line of demarcation between the various layers, which faded gradually into one another ; sometimes the greenish-blue layer was almost absent, especially when dezincification had been severe.

In most cases the scale, particularly the innermost layer, was very strongly adherent to the tube. Owing to the stratification, and the impossibility of removing the scale from the tube without introducing foreign matter, reliable quantitative analyses could not be made ; nor, probably, would they have been of much value, since the proportions of sand, ferric oxide, calcium carbonate (in the form of shell), &c., were obviously due to chance. These substances are always present in large and varying quantities, and effectually prevent any useful deductions being drawn from quantitative analyses of the scale.

In all cases in which a tube had suffered dezincification the greenish-blue layer was replaced, to a greater or less extent, by a white flocculent salt, which was found to be a basic chloride of zinc.

In one or two cases tubes were received partially choked with a loosely adherent deposit, light grey in colour. This was found to be principally sand, but contained also ferric oxide, magnesium salts, and calcium salts. Such tubes sometimes appeared to be more severely corroded than others taken from the same condenser, but not always.

One particularly interesting case came to hand. This was a 70 : 30 condenser tube taken from a Yarmouth trawler.

TABLE I.—*Collected Information from Inquiry Schedules.*

Business of Firm.	I. Length of Corroded Tube.	II. Normal Length of Service.	III. Percentage of Failures in Time stated in Column I.	IV. Length of Tube.	V. Position of Corrosion along Length of Tube.	VI. Position of Corroded Tubes in Condenser.	VII. Maximum and Minimum Temperature of Water leaving the Condenser.	VIII. Electric Lighting on Ship?	IX. Protective Measures.	X. Period of Run.	XI. Cause of Corrosion suggested by Firm.	XII. Nature of Deterioration.
	Years.	Years.		Ft. In.			° F.					
1. Shipping firm. (To Tropics.)	7½	15-20	6	12 9	Middle and inlet end.	Top nest of tubes.	110-116	Yes. S.*	Iron slabs.	12 days.	Tubes "not now made of the same clean alloy as formerly."	Dezincification.
2. Same as (1). Another ship.	15	15-20	19	15 8½	...	...	110-116	Yes. S.	Iron slabs.	12 days.	...	Thinning of tubes and pitting.
3. Shipping firm. (To Tropics.)	1½-2½	7-10	1·6	12 3	Inlet end.	...	70-110	Yes. D.	None.	...	Bad material used for tubes.	Dezincification and pitting.
4. Shipping firm. (Cross Channel.)	17	17	3·5	13 3½	Each end of tube.	Top nest of tubes.	85-110	Yes. D.	None.	22 hours.	Corrosion due to packing, which consisted of tallow-soaked cotton.	Thinning of tubes at ends and pitting.
5. Shipping firm. (General trade.)	3	7	...	13 1	Whole length of tube in pits.	Top nest.	about 100	No.	Cement wash put on doors of water spaces.	Various.	Defective manufacture of tube and galvanic action.	Dezincification and pitting.
6. Shipping firm. (Cross Channel.)	6	12	50	12 3	Ends of tube.	Bottom section.	90-102	Yes. D.	Zinc slabs.	Few hours.	No definite view.	Thinning of tubes and pitting.
7. Shipping firm. (Cross Channel.)	7	18-25	100	...	Whole length in pits.	General.	...	No.	Zinc slabs.	30-40 hours.	Absence of tin from the tubes.	Dezincification and pitting.
8. Shipping firm. Same as (7). Another ship.	11	20	Very high	11 4	General, but worst in middle.	General.	...	Yes. D.	Zinc slabs.	6 hours.	Local galvanic action due to settling of particles.	Dezincification and pitting.

9. Shipping firm. (Atlantic trade.)	11	11	High	13	8	At both ends.	General.	100-116	Yes. S.	Zinc slabs.	8 days.	Due to impingement of circulating water, but tubes are considered to have stood well.	Thinning and dezincification.
10. Same as (9). Another ship.	3	11	4·5	11	8¾	Near water inlet.	Bottom section.	68–102	Yes. S.	Zinc slabs.	7 or 31 days.	Local galvanic action.	Dezincification and pitting.
11. Same as (9). Another ship.	16	16	10	12	5½	4 in. from each end.	Varying.	69–93	Yes. S.	None.	…	[Life regarded as exceptionally good.]	Dezincification and pitting.
12. Shipping firm. (Cross Channel.)	4	…	100	…	…	Middle.	Through-out.	125–130	Yes. D.	None.	30 hours.	None suggested.	Dezincification and pitting.
13. Shipping firm (Tropics)	1	…	…	…	…	Middle.	Top section.	124	Yes. D.	None.	3 weeks.	None suggested.	Dezincification and pitting.
14. Shipping firm. (Atlantic.)	3¾	…	3·5	13	8½	Middle	…	90–107	Yes. D.	Harris-Anderson process. None.	…	None suggested.	Dezincification and pitting.
15. Shipping firm. (Tropics.)	7 (months)	…	1¼	…	…	Ends.	Bottom section.	100	Yes. D.	None.	Varying.	{ None suggested. Waterontsidetubes.	Thinning and pitting.

Land Installations.

	11	11	High	13	8	At both ends.	General.	100-116	Yes. S.	Zinc slabs.	8 days.		Thinning and dezincification.
16. Paper mill.	9 (weeks)	6-7	1¼	7	11	About 2 ft. from inlet.	Top section.	…	…	…	Continuous.	None suggested. Dock water used.	Dezincification and pitting.
17. Cotton mill.	4	7	…	…	…	Middle.	Near steam inlet.	75 85	…	…	11½ hours per day.	Due to acid in water from canal.	Pitting.
18. Electric power station.	8 9	…	2	9	6½	1 ft. from end to centre.	Various.	…	…	…	…	Fresh water used. None suggested. Brackish water used.	Dezincification and pitting.
19. Electric power station.	2	5	4	8	1½	Near ends.	…	…	…	Iron slabs.	Varying.	Bad quality of tubes. Fresh water used.	Dezincification and thinning at end.
20. Flour mill.	2	4	8	8	3½	Middle.	…	…	…	Zinc slabs.	Varying.	Bad quality of tubes and the sticking of bubbles of gas, especially CO_2, to tubes.	Dezincification and pitting.

* S. means single-wire system. D. means double-wire system.

Note.—Wherever blanks occur, no statement was inserted in schedule.

B

It had been in use twenty years, and was apparently as good as new. There was no sign whatever of dezincification or thinning. It was covered with a very hard uniform scale, with a looser finely reticulated surface layer. There was no well-marked blue-green layer, and this appeared to indicate that very little copper could have been removed from the tube, which, in fact, was practically as thick as when new.

The average total thickness of the scale was 0·31 millimetre, that of the hard lower layer being 0·13 millimetre. Analysis showed the latter to consist of oxides of copper and iron and calcium carbonate ; no zinc was present. Neither was there any zinc in the looser layer, which consisted of considerable quantities of calcium carbonate and sulphate, together with silica and oxides of copper and iron. The true thickness of the metallic portion of the tube was 1·29 millimetre, so that unless the tube had been originally of an unusual thickness—which is improbable—it had not lost more than 0·05 millimetre in twenty years.

Careful search was made among the deposits in badly corroded tubes for carbon particles. Although about a hundred cases were examined no such particles were ever found, and in no single instance could a dezincified spot or area be correlated definitely with such a particle. This, of course, does not prove that carbon in the form of graphite or coal had not started the dezincification of the tube, since it might subsequently have been removed when the tube was cleared by means of an iron rod or brush.

As a result of the study of the answers to the question-schedules, and of the tubes corroded under conditions of practical work, the authors came to the conclusions that few deductions of importance could be made, and that this method of work is only of value for indicating in a general way the nature of the problem to be attacked.

The chemical and physical conditions obtaining in condensers engaged in practical work are of a complex nature and may vary considerably from point to point, not only of the condenser as a whole, but even along each tube. Moreover, it is not usually possible to ascertain what are the exact conditions as regards such matters as temperature, speed of water, presence

of air, &c., in any particular plant. The possible variations in the conditions from part to part of the same condenser, which might be supposed to cause corresponding variations in the speed of corrosion, may be summarized as follows :—

1. *Variation of the water speed in different tubes.*—This may operate :—
      A. Directly as an independent effect.
      B. Indirectly as affecting 2.
      C. Indirectly as affecting 4.
2. *Variation in the temperature of the different tubes.*—This may operate :—
      A. Directly, owing to increased chemical activity.
      B. Indirectly, by removing gases from solution (see 6).
           Note.—Choked tubes may become highly heated.
3. *Variation in the distance of different tubes from electro-chemical protector blocks, bars, and main condenser bodies.*
4. *Variation in the distribution of solid substances which settle on the tubes.*
5. *Variation in the distribution and amount of water left in the tubes when the condenser is out of action.*
6. *Variation in the oxygen contained in solution in the water during its passage through the condenser.* The concentration will be highest where the water enters and lowest where it leaves the condenser.
7. *Variation in the quality of the water circulating through the tubes.*

Looking down this list, it becomes obvious that engineers in charge of condensers are not in a position to supply detailed information as to the exact nature of those conditions which may be expected to influence the course of corrosion.

Take, for instance, the distribution of temperature. The highest temperature will not necessarily occur at the middle of the top nest of tubes, where the steam usually enters the condenser. It will be influenced by the position and dimensions of baffle plates and by the speed of the water through the tubes. The speed of the water will not necessarily be the same through all the tubes, owing partly to the swirling action in the water ends, and partly to possible partial choking of certain tubes. In any given condenser, the distribution of temperature could only be ascertained by direct experiment ; and this is not possible without the employment of special apparatus.

Moreover, there is an almost entire lack of published experimental work giving quantitative measurements of the effect of these variations on the speed and nature of brass corrosion. Many opinions have been expressed in discussions on the

subject, but for the most part they have not been backed by experimental work. Arnold Philip * has on more than one occasion emphasized his view that electro-negative particles of carbon, &c., are of special importance in promoting corrosion, but does not appear to have brought forward any detailed experimental work to support it—perhaps because it seems to be such an eminently reasonable view. Bruhl † also neglected this point, and entirely failed to throw any light on the phenomenon of dezincification, which is the factor of principal importance in practical work. Moreover, with the exception of two experiments carried out at 40° C., he confined all his work to experiments at the ordinary temperature.

Milton and Larke ‡ carried out a considerable number of experiments to elucidate dezincification, but for the most part their work was confined to the electro-chemical aspect of the subject. Sinclair § also worked mainly along electro-chemical lines, but carried out a number of interesting experiments at temperatures higher than atmospheric. Tilden,‖ as long ago as 1886, observed the combined effect of ferric oxide and other substances and a temperature of 40° C. maintained for seven hours a day for eleven months, and probably succeeded in dezincifying his brass. He actually recorded his observations as " deposition of copper," but in view of the knowledge that has been accumulated in more recent years, it seems to the authors probable that he was really observing the phenomenon of dezincification. If this be so, he was probably the first experimenter to observe it in a laboratory experiment.

SECTION I.

Laboratory Investigation.

Owing to the fragmentary nature of the available experimental evidence, it was deemed advisable to arrange a some-

* *Journal of the Institute of Metals*, No. 1, 1911, vol. v. p. 99.

† *Ibid.*, 1911, vol. vi. p. 289.

‡ *Minutes of Proceedings of the Institution of Civil Engineers*, 1903, vol. cliv. pp. 138–189.

§ *Ibid.*, p. 184.

‖ *Journal of the Society of Chemical Industry*, vol. v. p. 84.

what extensive laboratory scheme for examining a few of the factors which seemed likely to bear upon the nature and speed of corrosion.

In the first place, it must be remembered that corrosion phenomena may be divided into two classes :—

1. The gradual wearing down of the tube, *i.e.* general corrosion in which copper and zinc are removed approximately in the proportions in which they occur in the alloy. This action will be called " complete corrosion."

2. Dezincification, followed by pitting, in which the zinc is removed preferentially, leaving a pit or area of copper-rich material. Such areas become quite weak and rotten, and in many cases the copper may easily be pushed out of the tube in the form of a plug, leaving a hole. These rotten tubes are no longer water-tight. The action which results in dezincification will be called " selective corrosion."

Practically all tubes suffer from the first form of corrosion, although it may be so retarded that the rate becomes practically zero. An instance of this has been cited already (p. 15).

" Complete corrosion " is sometimes more pronounced at the ends of the tubes, and may even give rise to perforation, but this is a comparatively rare phenomenon. Usually this type of corrosion is comparatively slow, and the vast majority of tubes fail owing to pitting induced by dezincification, before their strength has been seriously diminished by general attack.

It is, therefore, the problem of dezincification that has received the principal attention of the authors, and the problem of perforation by " complete corrosion " has not been specially investigated.

The view has sometimes been expressed that pitting by dezincification is merely ordinary corrosive action intensely accelerated locally, either by the action of electro-negative particles or in some other way. This view presupposes that the normal action of sea water on brass is a slow process of dezincification. The only experimental evidence on the point

appears to be that of Sexton,* who states definitely that when
70 : 30 brass is attacked by sea water, dezincification always
occurs.   However, this author gives only the very meagre
experimental details expected in magazine articles, and in
his book on corrosion they are repeated without addition.
It seemed, therefore, highly desirable to confirm or exclude
his conclusions, and this matter served as a starting point for
the laboratory research.

Experiments at Atmospheric Temperature, Series I.

The alloys selected for examination were four in number,
and were pieces of tube of the same batches as were used in
the large scale experimental plant, which will be described
later.   Analyses are given on page 57.   The tubes were sawn
in half and cut into 2-inch lengths, which corresponds to a
surface area of 4·2 square inches.   The Admiralty tube was
of smaller diameter, and hence surface area of 2-inch length
was less, $= 3·4$ square inches.   Their edges were filed smooth,
and a hole $\frac{1}{8}$ inch diameter was drilled near one end ; they were
cleaned and polished, and suspended in beakers by means of
glass hooks, as shown in Fig. 1, the top of the upper tube
being about $\frac{1}{2}$ inch and the lower tube about 3 inches below
the surface of the water.   Each beaker contained $1\frac{1}{2}$ litre of
natural sea water, the surface area of the water being $12\frac{1}{2}$
square inches.

In cleaning the tubes they were roughly polished on the
outside with fine emery paper to remove grease, oxide, &c.;
the inside surfaces were polished to a rather higher degree by
means of circular polishers rotated in a lathe.   The purpose
of this is explained later (see p. 31).   Every endeavour was
made to bring all the surfaces to the same degree of polish,
so that all the results obtained might be strictly comparable.

The experiments with these tubes served as a basis for the
examination of the effect of altering the various conditions
mentioned on page 19.   In these experiments the speed of
the water was zero.   The temperature was the ordinary tem-

* *Engineering Magazine*, vol. xxx. 1906, and " The Corrosion and Protection of
Metals " (Scientific Publishing Co.), p. 116.

perature of the laboratory, averaging 18° C. to 20° C. No protecting metals or electro-negative particles were present. Normal sea water, taken at high tide outside the port of Liverpool, was used. The oxygen content was simply that which could diffuse down to the tubes from the surface of the water, free access of air to the beakers being allowed—they were only loosely covered with large sheets of coarse filter paper to keep out dust, &c. The concentration of the sea
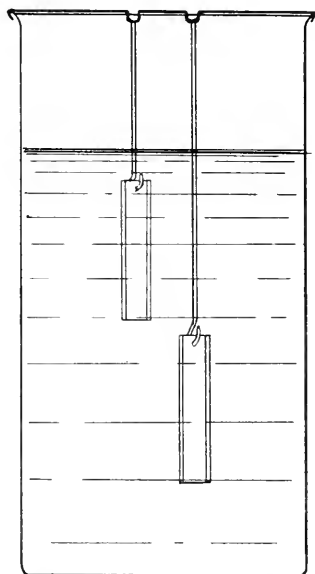
Fig. 1.—Mode of Immersion.   Vertical Tests.

water was kept constant by adding distilled water from time to time to make good the loss by evaporation.

The tubes were accurately weighed before examination, and at the end of fifteen days were removed, well cleaned by means of a rubber-tipped glass rod, and all loose deposit removed. They were then carefully dried and weighed. They were re-immersed, and further weighings made from time to time. The results are recorded in Tables II. and III., and in graphical form in Figs. 2 and 3. The sea water was renewed periodically as indicated in the tables.

Table II.—*Sea Water Corrosion Results. 1st Series. Upper Tubes.*

Composition of Tube.	Interval.	1. 70 : 30	2. 79 : 28 : 2	3. 61 : 39	4. 70 : 29 : 1
Initial weight in grammes . . Weight after corrosion for . . Loss in grammes . . . . Percentage loss	... 15 days	14·4576 14·7450 0·0126 0·08	14·4914 14·4769 0·0145 0·10	14·9114 14·9034 0·0080 0·05	10·8808 10·8666 0·0142 0·13
Weight after . . . . Percentage loss	22 days ...	14·7380 0·13	14·4724 0·13	14·9018 0·06	10·8624 0·17
Weight after . . . . Percentage loss	28 days Sea water renewed	14·7330 0·17	14·4674 0·17	14·9020 0·06	10·8585 0·20
Weight after . . . . Percentage loss	84 days Sea water renewed	14·7100 0·32	14·4372 0·37	14·8870 0·16	10·8204 0·55
Weight after . . . . Percentage loss	168 days Sea water renewed	14·6910 0·45	14·4126 0·54	14·8720 0·26	10·7842 0·89
Weight after . . . . Percentage loss	208 days ...	14·6840 0·50	14·4030 0·61	14·8645 0·31	10·7680 1·04

Note.—Owing to the slowness of the attack on the metal, and the slowness of the consequent diminution in concentration of the sea water, long intervals were allowed to lapse before renewal

Table III.—*Sea Water Corrosion Results. 1st Series. Lower Tubes.*

Composition of Tube.	Interval.	1. 70 : 30	2. 70 : 28 : 2	3. 61 : 39	4. 70 : 29 : 1
Initial weight in grammes . Weight after corrosion for . Loss in grammes Percentage loss .	... 15 days	14·4352 14·4235 0·0117 0·08	15·6184 15·6050 0·0134 0·09	15·1424 15·1335 0·0089 0·06	11·6314 11·6174 0·0140 0·12
Weight after . . . . Percentage loss	22 days ...	14·4192 0·11	15·6000 0·12	15·1330 0·06	11·6130 0·16
Weight after . . . . Percentage loss	28 days Sea water renewed	14·4148 0·14	15·5932 0·16	15·1330 0·06	11·6092 0·19
Weight after . . . . Percentage loss	84 days Sea water renewed	14·3966 0·27	15·5636 0·36	15·1202 0·15	11·5734 0·50
Weight after . . . . Percentage loss	168 days Sea water renewed	14·3772 0·40	15·5404 0·50	15·1066 0·24	11·5318 0·86
Weight after . . . . Percentage loss	208 days ...	14·3705 0·45	15·5130 0·55	15·1010 0·27	11·5130 1·02

· In conducting such experiments as these, it has been found necessary to take into account the following factors :—

    A. The volume, concentration, and temperature of the corroding medium.

    B. The mode and depth of immersion.

VERTICAL IMMERSION TESTS.
UPPER TUBES.
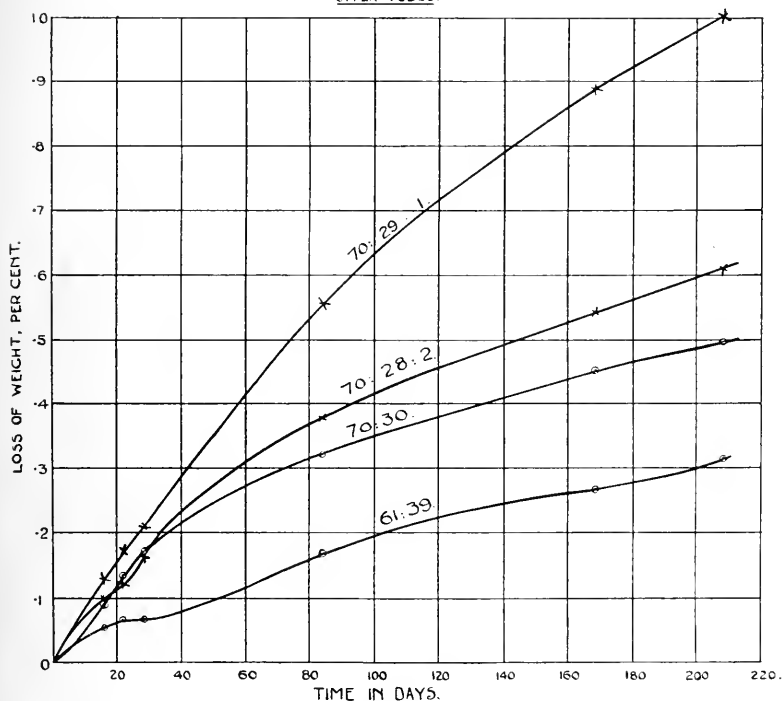
Fig. 2.

    C. The rate of diffusion, whether natural or stimulated artificially by stirring, &c.

    D. If diffusion be natural, the superficial area of the sea water surface becomes a factor.

    E. Area of exposed surface of corroding metal.

    F. The condition of the surface of the corroding metal.

All these factors have been taken into account in the experiments described, and have been kept similar for all

tests in each series of experiments. The omission to state
their experimental conditions in their published accounts is
no doubt responsible for the conflicting results obtained by
previous workers.

VERTICAL IMMERSION TESTS.
LOWER TUBES.
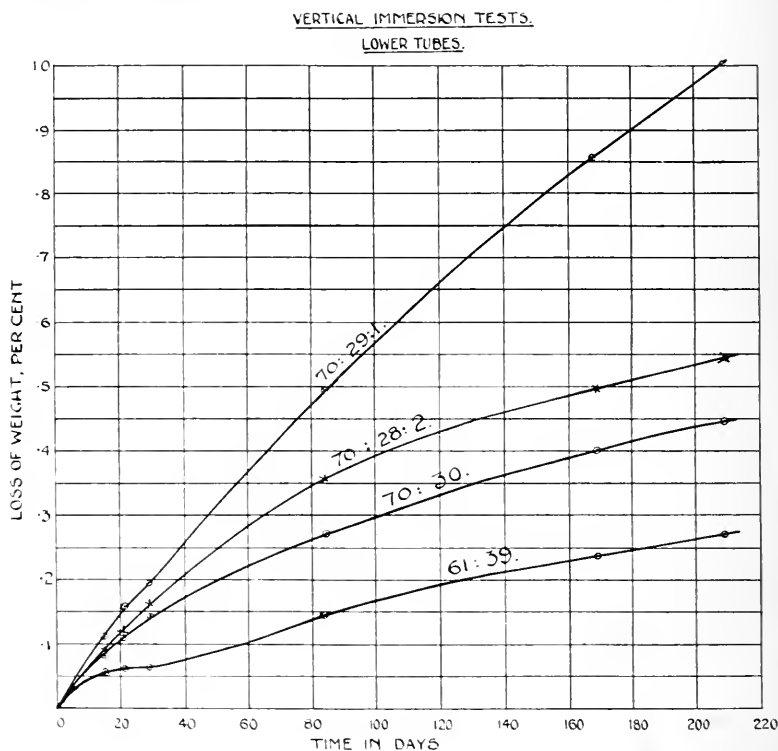
FIG. 3.

General Features of the Phenomena observed.—It soon became
clear that the first stage in the corrosion of brass is the
oxidation of one or both of the constituent metals. Cohen
and others have shown that in the absence of oxygen no
corrosion will take place, and the authors have confirmed this
fact. The earliest visible sign of corrosion is the formation of
a layer of brown oxide on the surface of the specimen.
Whether or not the oxidation is direct is not a question of
importance for the purposes of this paper.

On either view the net result is the same, namely, that the

alloy becomes gradually covered with a layer of oxide. This layer is very tenacious, and is not removed by ordinary rubbing with a rubber-tipped glass rod. In the case of 70 : 30 brass, it is of a reddish-brown colour, darkening to a brownish-black as time goes on.

The thickness of this layer of oxide is a matter of some importance, as it affects to a certain extent the accuracy of the loss of weight method of estimating corrosion. Careful micrometer measurements have shown that it varies from 0·01 millimetre in thickness after a few months' immersion, to about 0·04 millimetre after nine months. The losses of weight given in all the tables in this paper refer to measurements made with this layer of oxide left adhering to the tubes in an unbroken state, except where the contrary is stated.

An objection may be raised that this layer of oxide should have been removed by reduction in hydrogen before the final weighing. In some attempted measurements of the thickness of the oxide layer this procedure was carried out, but the results were not satisfactory. The reasons for this were—(1) that zinc oxide is not reduced at moderate temperatures, and (2) that some zinc was volatilized in the stream of hydrogen gas. As a result the light powder found on the tube at the end of the experiment was not pure copper and zinc oxide, but finely divided brass, and the loss of weight when this was removed was too great.

After trying a number of alternative methods, such as measuring the reduction of tube thickness and the diminution of the chlorine content of the sea water, the conclusion was reached that the most accurate and satisfactory comparative results would be obtained by weighing all the specimens after corrosion with the oxide layer left unbroken.

It was noticed that the formation of oxide did not take place uniformly over the whole surface of the tube. It started at certain areas, irregular in distribution and shape, which could not be correlated with the individual crystals of the metal. The layer gradually spread until it covered the whole of the surface of the tubes.

It may be of interest to mention here that Lambert,* working with a sample of metallic iron which was probably the

* *Journal of the Chemical Society*, October 1912, p. 206.

purest and most homogeneous metallic substance of any kind
that has ever been prepared, showed that even in this case
oxidation began at certain spots and then spread outwards.
The same result may be observed if a piece of brass tube be
heated in a hot-air oven till the surface begins to oxidize.
It is evident, therefore, that the very minutest differences,
chemical or physical, in a metal will determine the points
at which oxidation begins, but, according to the experiments
of the authors, it does not necessarily follow that subsequent
corrosive activity will be most pronounced at these same points.

The tubes become tarnished when they have been immersed
in water for only a few hours, and a slight bluish opalescence
becomes observable in the water.   In the course of two or
three days a deposit settles to the bottom of the beakers in
the form of a fine greenish-blue powder.   In the case of
Muntz metal the deposit is paler in colour, and the surface of
the metal exhibits a sallow yellowish tint instead of the reddish-
brown colour exhibited by the other tubes.   The tubes undergo
no further change in appearance, but the gradual increase in the
amount of deposit shows that the oxide layer is being continu-
ally removed and reformed.   It appears to be removed by a
reaction with the sodium chloride of the sea water, whereby
insoluble basic chlorides of copper and zinc are formed.

In certain experiments the greenish-blue deposit was col-
lected and analysed, and was found to contain the whole
of the copper that had been removed from the brass, and
a large part of the zinc.   The remainder of the zinc was
present in solution as zinc chloride.

The copper and zinc are attacked in approximately the
proportions in which they occur in the alloy.

The fact that copper is entirely absent from the liquid
suggests that the cuprous oxide first formed reacts with the
chlorides present in the sea water, forming cuprous chloride
or oxychloride.   These, being highly insoluble in sea water,
are instantly precipitated, thus accounting for the fine bluish
opalescence produced so soon after corrosion has started.   On
the other hand, only part of the zinc forms an insoluble basic
chloride, and part remains in solution as normal zinc chloride.
As corrosion proceeds, the sea water becomes slightly alkaline,
due to the removal of carbon dioxide, which appears to be

carried down in the form of basic carbonate. On these views the greenish-blue deposit will be a mixture of basic carbonates and chlorides of copper and zinc, its exact composition varying according to prevailing conditions.

As a check on the validity of these views, it was thought desirable to ascertain whether any reaction would take place between sea water and the oxides of copper and zinc prepared by ordinary chemical means. Accordingly, pure cuprous oxide was prepared by the addition of glucose to pure copper sulphate in the presence of tartaric acid. The resulting fine bright-red oxide was placed in a porcelain dish in contact with sea water. No signs of reaction were noticeable for about three weeks, after which time the greenish-blue salt began to make its appearance.

Some of the oxide was then placed in a beaker of sea water suspended in a thermostat at $40°$ C. After two or three days the blue salt, which characterizes the ordinary process of general corrosion, made its appearance.

In view of these results and of the fact that the blue salt is readily formed in all ordinary cases of corrosion at the ordinary temperature, a fresh batch of cuprous oxide was made with a view to ascertaining whether the details of preparation had any effect on the speed of reaction. In this case the oxide was made from pure copper sulphate and glucose without the addition of tartaric acid. The resulting oxide was lighter in colour and had a yellowish tinge. In this state the oxide readily reacted with the sea water at the ordinary temperature, with the formation of the greenish-blue basic salt in the course of a few days.

It was thought desirable to ascertain the composition of the deposit, and for this purpose a suitable quantity was prepared by leaving several feet of $70:30$ tube in contact with 4 litres of sea water for several months. The salt does not adhere at all tightly to the tubes, and was washed off, dried, weighed and analysed. The result was as follows:—

	Per Cent.
Copper	40·42
Zinc	13·02
Chlorine	2·95
Carbon dioxide	4·20

Balance, oxygen, magnesium, and calcium salts and insoluble matter.

It is evident that the salt is a double basic chloride and carbonate of copper and zinc. It is noticeable that it contains less zinc proportionally to the copper than the original tubes. This is due to the fact that in this and all other experiments on corrosion described in this paper, a part at least of the zinc remains in solution as zinc chloride. The nature of corrosive action in stagnant sea water at the ordinary temperature, and, as will be shown subsequently, at somewhat higher temperatures, may now be summarized as follows :—

1. The *oxygen in solution* * reacts with the copper and zinc of the alloy, producing cuprous oxide and zinc oxide. These substances form first at certain areas, and constitute a brown or reddish layer which darkens in time (probably owing to the formation of cupric oxide), and which finally completely covers the tube.

2. The oxide layer reacts with the sodium chloride and carbon dioxide of the sea water, the metals thus passing into solution, but instantaneously the whole of the copper and a large part of the zinc are precipitated in the form of a greenish-blue basic salt which is insoluble in sea water, and is usually deposited in a flocculent or non-adhesive state on the tube. The remainder of the zinc remains in solution as chloride.

3. The reaction between the oxide and the sea water probably proceeds at about the same rate as the formation of the oxide, since the oxide layer is always found beneath the greenish-blue salt, but yet only increases very slowly in thickness. Owing to this reaction, the sea water gradually becomes alkaline because of the removal of carbon dioxide.

4. If the tube be allowed to dry, or if the green salt be allowed to remain on the tube for several months, the salt will stick tightly to the tube, but in the latter case only in small isolated patches.

5. The sticking of the salt interferes with the accuracy of loss-of-weight experiments if carried out for very long periods. If violent measures are taken to remove the green salt, the oxide layer beneath is also removed in patches.

* It is only the oxygen *in solution* that reacts with the brass, not oxygen in the free gaseous condition.

6. The experiments described above have been carried out for a period of eight months, and no signs of selective corrosion or local action have been observed. The tubes present a perfectly uniform oxidized appearance indicating progress of complete corrosion only.

In view of the widely held opinion that "spills" and "flaws" on the interior surfaces of condenser tubes form corrosion centres and start pitting, the inside surfaces of the tubes used in Series I. experiments were highly polished, as described previously. The original intention was to examine the polished surfaces under the microscope from time to time as corrosion proceeded, and to try and observe in this way whether corrosion was being accelerated in the neighbourhood of any flaws. Microscopic observation of the metal is effectually prevented by the interposition of the oxide film. Still no evidence was found by this or any other means to show that flaws had any influence on sea water corrosion at the ordinary temperature.

In view of the fact that sea water always contains a considerable quantity of dissolved carbon dioxide, it was thought desirable to ascertain the effect of this substance apart from the presence of salt. Accordingly the following experiment was made:—

A 3-inch length of $70:30$ tube was suspended in $1\frac{1}{2}$ litre distilled water, which was maintained saturated with CO_2 by bubbling a slow stream of the gas through the liquid. The tube was weighed before and after the experiment, which lasted sixty-four days.

		Grammes.
Weight before experiment	.	$21\cdot0372$
„ after 64 days	.	$20\cdot9450$
Loss of weight	.	$0\cdot0922$
Percentage loss	.	$0\cdot4382$

At the conclusion of the experiment the tube presented a dull purplish colour, but none of the usual blue-green salt could be seen. The liquid remained clear, but on filtering a trace of green deposit was found. Yet the above result shows that quite a considerable amount of metal was removed, indeed more than in the case of a similar tube immersed in sea water for the

same length of time.   Obviously the metal removed must
have remained in solution.   This was borne out by the observa-
tion that on heating the clear liquid to boiling, a flocculent
white precipitate of basic zinc carbonate was formed.   The
important point of this experiment is that the loss of metal
is almost entirely concentrated on the zinc.   It should be
mentioned, however, that this form of dezincification takes
place uniformly over the whole of the brass, and in this respect
is to be distinguished from the type of dezincification referred
to later in this paper as " selective corrosion."   Nevertheless
the experiment indicates that waters highly charged with
carbon dioxide gas must have a serious effect on brass.

Discussion of Results of Experiments in Series I.

Comparison between the results obtained for the upper and
lower tubes in the same beakers reveals the fact that in all
cases the upper tubes have suffered greater loss in weight.
This is only to be expected, since oxygen is an important
factor in corrosion phenomena, and is constantly being removed
by reaction with the metals of the tube.   It can only be re-
placed by diffusion from the surface of the liquid, and the
new supplies will necessarily reach the upper tubes first.
Otherwise the results obtained for the upper and lower tests
are in good agreement with one another.

Figs. 2 and 3 show clearly that the Muntz metal tubes
have lost least in weight.   Of the others, the $70:29:1$ alloy
shows the lowest resistance to complete corrosion, whereas
the $70:30$ and $70:28:2$ alloys behave nearly alike and are
rather more resistant.   In all cases the rate of corrosion de-
creases gradually with lapse of time.

These results are surprising.   In the first place, it would
be expected that the Muntz metal tube would suffer the
greatest loss in weight, since it is a two-phase system, and
would therefore appear to be peculiarly liable to electro-
lytic action.   The $70:29:1$ metal and the $70:30$ brass are
homogeneous single-phase systems and would be expected to
show less loss of weight.   The $70:28:2$ tubes contained
a small amount of free lead interspersed between the crystals

in a fairly regular manner, and from the electro-chemical point of view might be expected to show a loss of weight intermediate between the Muntz metal and the $70:30$ brass.

It is evident that the order of corrodibility of these tubes differs widely from that which would be predicted from the electro-chemical point of view, and the authors conclude that electro-chemical action between the various phases is not an important factor in determining the amount of complete corrosion under the conditions employed in these experiments. The reason for this appears to be that the adherent oxide film, which covers the whole surface of the tubes soon after they have been exposed to the sea water, interposes a considerable resistance into any electrolytic circuit which may at first be formed between the different phases. Consequently the effect of the juxtaposition of two or more phases is completely masked by other factors which influence the speed of corrosion.

Second Series of Experiments.

In view of the unexpected results obtained in the first series of experiments, it was decided to repeat them with slight modifications. The differences consisted in the use of 3-inch * lengths of tube suspended in the beakers horizontally instead of vertically, so that a deposit might rest on the tube instead of falling to the bottom of the beaker, and secondly, in suspending the tubes by means of white string from glass rods laid on the top of the beakers, as shown in Fig. 4. The second modification was merely for the sake of convenience, but the first was carried out to test the effect of the presence of the blue salt on the speed of corrosion. In the first series of experiments this salt fell to the bottom of the beaker, in the second it remained *in situ* on the tubes. Two tubes of the same kind were immersed in each beaker at the same depth (approximately 1 inch below surface of water), otherwise the experiments were carried out in an exactly similar manner to Series I. The results of this series of ex-

* The surface area of a 3-inch length of tube is 6·4 square inches=40 square centimetres. For the $70:29:1$ tube=4·9 square inches or 30·5 square centimetres. In all other experiments described 3-inch lengths were used.

periments are given in Table IV., and the results are plotted
in Fig. 5.

It will be seen that while the differences in the speeds
of corrosion between the various tubes are not so marked
as in the first series of experiments, yet the rates of corrosion
are in the same relative order, Muntz metal again showing
the least loss of weight and the 70 : 29 : 1 alloy the most.

The losses of weight recorded in this series of experi-
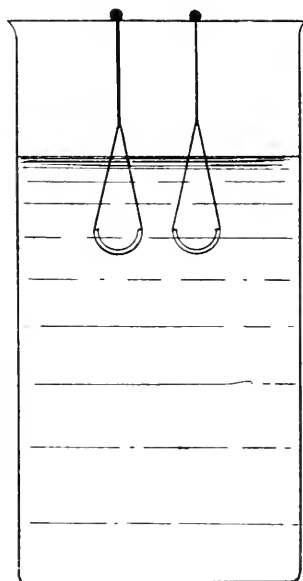
Fig. 4.—Mode of Immersion.   Horizontal Tests.

ments are greater than in the first series.   The differences
are not great, and may be accounted for by the fact that the
whole length of the tube was nearer the surface of the water
than the average distance in the case of the vertical tubes.
It seems unlikely that the presence of the blue salt has any
important effect on the rate of corrosion of the tubes.

It has been suggested from time to time by engineers and
others that sea water remaining stagnant in the tubes has
a specially rapid corroding effect on them.   The second series
of experiments shows that a 70 : 30 brass tube loses about

TABLE IV.—*Sea Water Corrosion Experiments. 2nd Series.*

	Interval.	1. 70:30 A.* (Horizontal.)	1. 70:30 B. (Vertical.)	2. 70:28:2 A.	2. 70:28:2 B.	3. 69:31 A.	3. 69:31 B.	4. 70:29:1 A.	4. 70:29:1 B.
Initial weight in grammes	...	22·3662	22·8080	23·6705	23·5400	22·5950	22·7008	15·9360	16·1428
Weight after corrosion for	30 days	22·3122	22·7625	23·6242	23·4954	22·5760	22·6812	15·9000	16·1087
Loss in grammes	...	0·0540	0·0455	0·0463	0·0446	0·0190	0·0196	0·0360	0·0341
Percentage loss	...	0·24	0·20	0·20	0·19	0·08	0·08	0·22	0·21
Weight after	Sea water renewed 60 days	22·2910	22·7444	23·5955	23·4662	22·5560	22·6628	15·8774	16·0878
Percentage loss	...	0·34	0·28	0·32	0·31	0·17	0·17	0·36	0·34
Weight after	Sea water renewed 90 days	22·2700	22·7225	23·5695	23·4418	22·5350	22·6428	15·8565	16·0675
Percentage loss	...	0·43	0·38	0·43	0·42	0·26	0·25	0·50	0·47
Weight after	Sea water renewed 120 days	22·2270	22·6800	23·5365	23·4100	22·5110	22·6200	15·8350	16·0450
Percentage loss	...	0·62	0·56	0·56	0·55	0·37	0·36	0·63	0·61

* The tube-pieces A and B belonging to Tube 1 were immersed in same beaker in different ways—A horizontally and B vertically, and this is reflected in the results.

0·6 per cent. of its weight under the action of sea water for four months at the ordinary temperature. Supposing no pitting to take place, and assuming that a tube could be used

HORIZONTAL IMMERSION TEST.
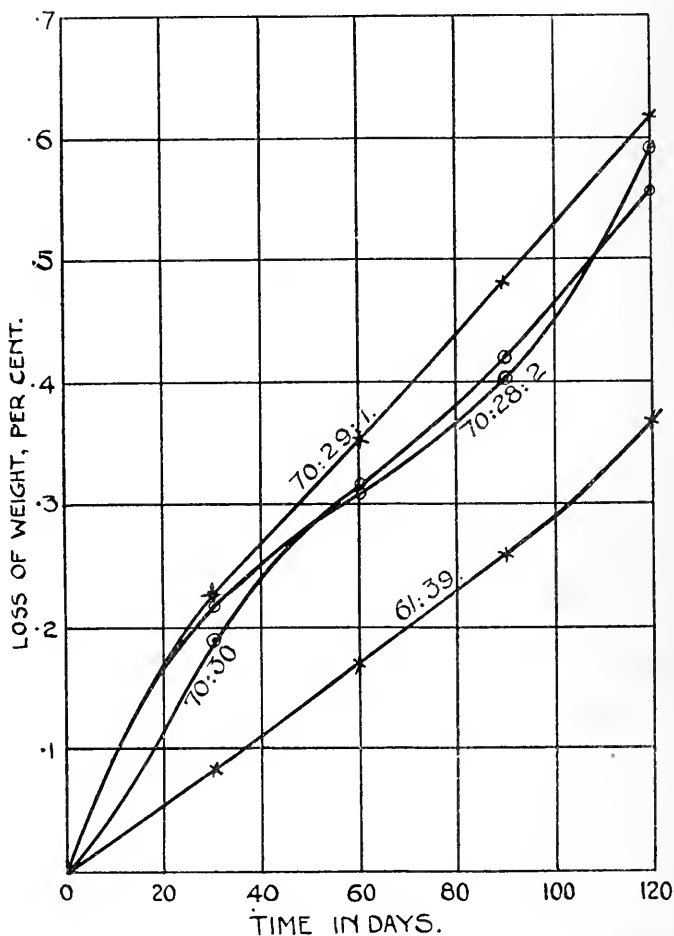
FIG. 5.

till it had lost two-thirds of its thickness, that corrosion takes place on one side only of the tube, and that it proceeds uniformly at the same rate, the life of a 70 : 30 tube should be

about seventy-five years. In practice the life of a tube rarely reaches twenty-five years, and the normal life of a tube may be taken to be about twelve years under average conditions.

As a matter of fact, the life of a tube in practice is usually limited, not by its resistance to thinning, but by local dezincification and pitting. Only complete corrosion occurred in these two series of experiments, and therefore the experiments hitherto described throw but little light on the practical problem, except by showing that stagnant sea water at the ordinary temperature is not of itself an important source of trouble.

Influence of Concentration of Sea Water.—Condenser tubes are occasionally submitted to the action of sea water containing salts of a different concentration from the normal. Thus when sailing up rivers and estuaries, the water pumped through the condensers may contain much less salt than water from the open sea. On the other hand, drops of water may lie along the bottom of the tubes when the condenser is out of action and partially evaporate, giving rise to a concentrated solution of sea water salt. Further, such drops of concentrated sea water may be formed always in the same positions in the tubes. Consequently it was thought desirable to obtain data showing the effect of these factors.

The experiments were carried out as before, with the exception that the liquid used was sea water which had been concentrated to $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$ of its original volume, and a fourth test was made with sea water which had been diluted to twice its volume with distilled water. Thus calling the concentration of ordinary sea water 1, the concentration of the liquids used could be denoted by 4, 2, 1·5, and 0·5 respectively. Only one kind of tube was used in the experiments with concentrated sea water, viz. 70 : 30 brass. Two tubes were immersed horizontally in each kind of sea water exactly as in Series II. The results are shown in Table V. and Fig. 6.

It will be seen that, in general, an increase of concentration gives an increase in the rate of complete corrosion. Between sea water of concentrations 1 and 1·5 there is little difference in rate of attack, but the higher concentrations 2 and 4 accelerate it to almost twice the ordinary rate. The corrosion pro-

Table V.—Concentrated Sea Water Corrosion Experiments.

	Interval	No. 1 in 4 litres ordinary Sea Water.		No. 1 in 1½ litre Sea Water of Concentration 1.5.		No. 1 in 1½ litre Sea Water of Concentration 2.		No. 1 in 1½ litre Sea Water of Concentration 4.	
		A.	B.	L.	L.	K.	L.	M.	O.
Initial weight in grammes	...	20·5590	20·1850	22·7810	22·9680	20·8436	20·9360	21·3894	21·7851
Water after corrosion for	30 days	20·5158	20·1406	22·7312	22·9222	20·7840	20·9065	21·3280	21·7151
Loss in grammes	...	0·0432	0·0444	0·0498	0·0458	0·0596	0·0635	0·0614	0·0703
Percentage loss	...	0·21	0·22	0·22	0·20	0·29	0·33	0·29	0·32
Weight after	Sea water renewed 60 days	20·4961	20·1218	22·7054	22·8882	20·7418	20·8925	21·2794	21·6578
Percentage loss	...	0·31	0·31	0·33	0·30	0·49	0·53	0·52	0·58
Weight after	Sea water renewed 90 days	20·4576	20·0658	22·6840	22·8740	20·7068	20·8875	21·2286	21·6428
Percentage loss	...	0·49	0·49	0·43	0·40	0·66	0·70	0·75	0·84
Weight after	Sea water renewed 120 days	20·4125	20·0510	22·6555	22·8385	20·6670	20·8510	21·1730	21·5530
Percentage loss	...	0·71	0·67	0·55	0·56	0·85	0·88	1·01	1·06

duct was the ordinary blue deposit already described. No signs of dezincification were observed.

RATE OF CORROSION BY CONCENTRATED SEA WATER.
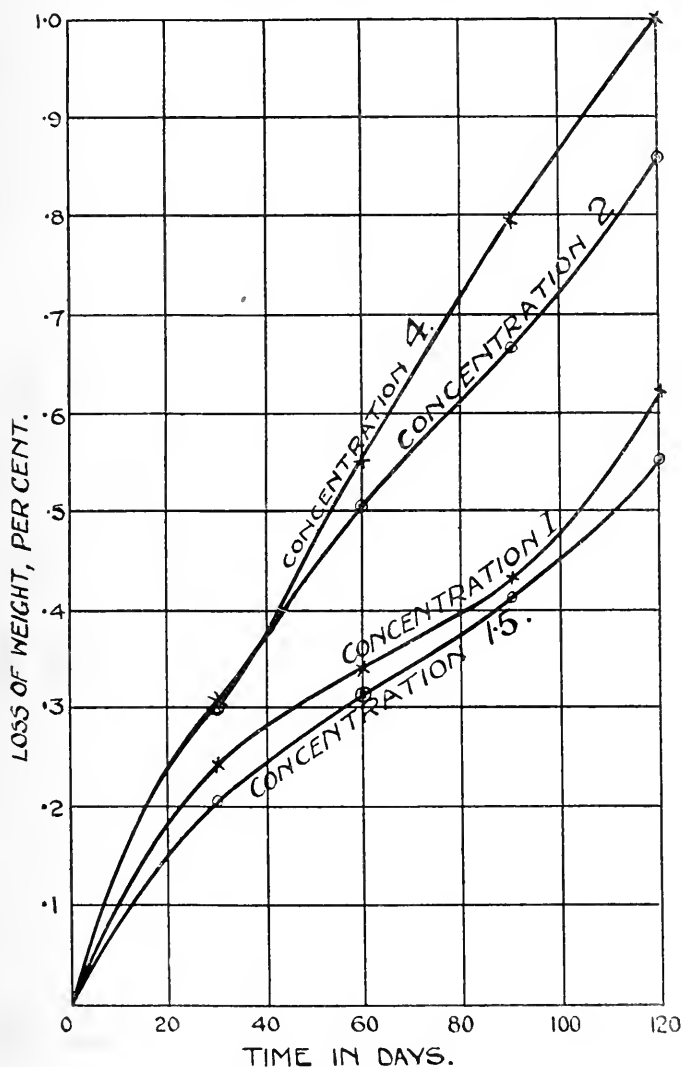
FIG. 6.—Influence of Sea Water Concentration.

There was a noticeable difference from the usual appear-

ance in the case of the tubes which were corroded in the
highly concentrated sea water.   The oxide layer was much
lighter in colour ; and the greenish deposit adhered to the
tubes tightly in patches, rendering the loss of weight values
less accurate.   The deposit on the other hand was more
highly coloured, indicating that there was less copper in the
oxide layer, but more in the deposit.

A series of tests with the four types of tube suspended
vertically (using 2-inch lengths), precisely similar to Series I.
experiments, was carried out in diluted sea water (concentra-
tion 0·5).   The results obtained for the upper tubes are given
in Table VI. and Fig. 7.

TABLE VI.—*Diluted Sea Water Corrosion Tests.*

	Interval.	**1.** 70 : 30	**2.** 70 : 28 : 2	**3.** 61 : 39	**4.** 70 : 29 : 1
Initial weight in grammes	...	12·1652	13·8800	13·3290	9·6500
Weight after corrosion for	28 days	12·1514	13·8668	13·3197	9·6408
Loss in grammes . .	...	0·0138	0·0132	0·0093	0·0092
Percentage loss . . .	... Sea water renewed	0·11	0·095	0·07	0·095
Weight after	84 days	12·1274	13·8415	13·3044	9·6172
Percentage loss . . .	... Sea water renewed	0·31	0·28	0·18	0·34
Weight after	168 days	12·0960	13·8150	13·2895	9·6000
Percentage loss . . .	...	0·57	0·47	0·30	0·52

They show that a decrease in the concentration of the sea
water diminishes slightly the rate of complete corrosion.   A
complicating factor, however, is introduced by the fact that
after the lapse of five to six months a new type of corrosion is
observed to set in.   The tubes (with the exception of the
70 : 28 : 2 alloy) which had hitherto undergone only ordinary
complete corrosion of the kind previously described became
covered (mostly on the backs) with minute specks of a white
substance, which was strongly adherent.   When the white salt
was removed, a coppery area was invariably disclosed.   Evi-

dently the corrosion is proceeding in a different manner from usual, and is of the type characterized in this paper as " selective." This aspect of corrosion is dealt with in detail later.
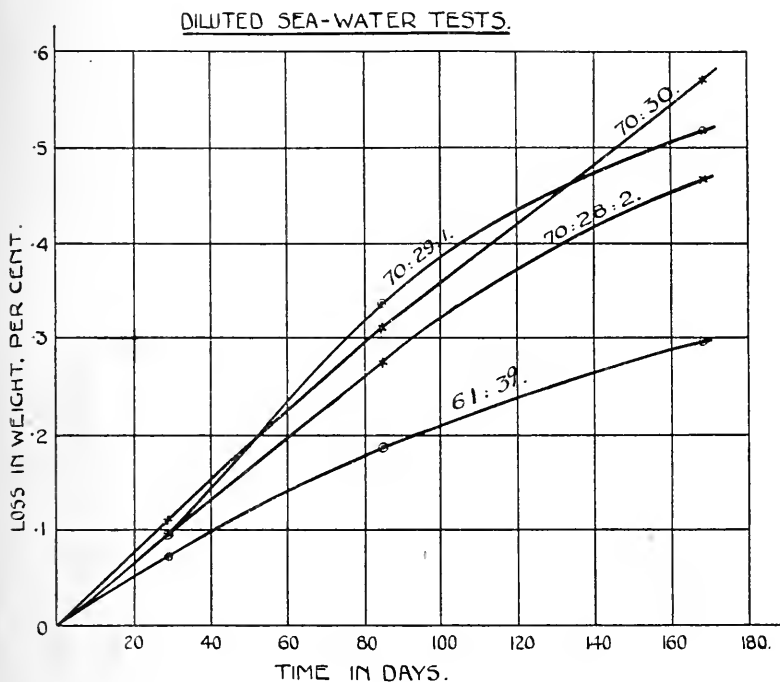
FIG. 7.

It is very noteworthy that the 70 : 28 : 2 brass did not show any sign of this selective attack under these conditions, while of the others Muntz metal seemed to be the most susceptible to it.

INFLUENCE OF PARTICLES.

The opinion has been repeatedly expressed by speakers and writers on corrosion that trouble occurs most frequently in practice when sea water has been allowed to remain at rest in the tubes. Arnold Philip, in particular, has suggested that stagnant sea water gives rise to serious corrosion, but acts principally by allowing particles of carbon and other electro-

negative bodies to remain at rest in one position on the tube, thus giving rise to intense local electro-chemical action.

In the early stages of the research, it seemed to the authors probable that some such action might be the cause of the dezincification of tubes, and experiments were arranged to test the effect of the following substances, acting in conjunction with stagnant sea water at atmospheric temperatures :— Graphite, coal, coke, clinker, sand, iron pyrites ; loss-of-weight experiments were carried out in exactly the same manner as in Series II. experiments previously described, the various substances being placed on the tubes, which were all of the 70 : 30 type. In the case of coal, coke, &c., the materials were tied firmly down to the tubes, so as to touch them at certain definite points. Check tubes, *i.e.* tubes without any substance in contact with them, were placed in the same beakers with the tubes being tested. The results are collected in Table VII. (p. 43).

These results show that none of the substances examined exert any important influence on the amount of general corrosion at the ordinary temperature. Moreover, the most careful scrutiny of the tubes failed to reveal any sign of dezincification. In general, the effect of these substances was to retard slightly the speed of corrosion. Under the graphite and sand the tubes were quite bright and unoxidized, and it seemed that the only effect of these substances was a mechanical one, whereby free access of oxygen to the tube was prevented. It seemed just possible that the bright areas of the tubes were really areas of most active attack, from which oxide was removed more rapidly than it was formed, but careful micrometer measurements showed that in every case tubes were slightly thicker at the bright areas than at the surrounding parts.

These experiments as regards the effect of graphite were repeated with pieces of Admiralty tube, and exactly similar results obtained.

It seemed probable that the failure of such substances as graphite and coal, even when in close contact with the tubes, to promote corrosion, was due to the resistance interposed in the electrical circuit at the point of contact between the tube

TABLE VII.—*Influence of Particles and Deposits on Sea Water Corrosion.*

Details of Treatment.	Interval.	Weight Before.	Weight After.	Loss.	Percentage Loss.	
		Grammes.	Grammes.	Grammes.		
1. 70·30 tube alone in 1½ litre sea water immersed horizontally (check)	30 days	21·4372	21·3210	0·1162	0·54	*Check*
2. Tube similar to above in 1½ litre sea water with pieces of graphite and coke tied on to interior surface	30 days	22·1156	22·0600	0·0556	0·25	*Graphite* and *Coke*
3. Tube treated similarly with pieces of clinker and iron pyrites on surface	30 days	20·9535	20·8752	0·0783	0·37	*Clinker* and *Pyrites*
4. Check tube . . .} both immersed in 1½ litre sea water on surface Tube with sand laid	45 days	18·5483 18·4648	18·5098 18·4352	0·0385 0·0296	0·21 0·16	*Check* *Sand*
5. Check tube . . .} both immersed in 1½ litre sea water Tube in contact with freshly prepared Fe₂O₃	8 days	20·2756 20·4870	20·2590 20·4641	0·0166 0·0229	0·08 0·11	*Check* *Fe₂O₃* (fresh)
6. Check tube . . .} both placed horizontally in sea water Similar tube and ignited Fe₂O₃	15 days	18·4078 18·4648	18·3814 18·4300	0·0264 0·0348	0·14 0·19	*Check* *Fe₂O₃* (ignited)
7. Check tube . . .} both immersed horizontally in 1½ litre sea water Tube with deposit formed on surface by evaporation of sea water at ordinary temperature	45 days	18·8646 21·4256	18·8115 21·3240	0·0531 0·1016	0·28 0·42	*Check* *Sea water deposit*
8. Tube with sea water deposit formed as above but then baked for 9 hours at 55° C. Tube with sea water deposit baked 9 hours at 100° C. } both placed in 1½ litre sea water	45 days	19·6042 19·6608	19·4955 19·5440	0·1087 0·1168	0·55 0·59	*Baked deposit 55°* *Baked deposit 100°*

and carbon. To test further the efficacy of electro-chemical action the following experiment was also made :—

A circular hole was bored in a piece of 70 : 30 brass tube, and a piece of copper rod was screwed into it, thus ensuring a thoroughly satisfactory electrical contact between the electro-negative copper and the electro-positive brass. The tube was then immersed in stagnant sea water for sixty days, together with a check tube. The results of loss-of-weight determinations were as follows :—

<div align="center">

Loss after 60 Days =

Copper Plug Tube.	Check Tube.
Per Cent.	Per Cent.
0·23	0·25

</div>

There was no sign whatever of any localized reaction on the brass surrounding the copper, such as would have occurred if any electro-chemical stimulation of corrosion had taken place. The conclusion to be drawn from this and other experiments to be described subsequently is that, even under the most favourable conditions that can be devised to exhibit electro-chemical attack on brass by carbon and copper, no such action takes place, and that in consequence the settling of particles on condenser tubes is not *per se* a cause either of dezincification or of any intense local complete corrosion inducing a pit.

The authors attribute the absence of such action to the contact resistance interposed in the electrical circuit by the adherent oxide film which forms on the surface of the brass.

The existence of electro-chemical action, which a number of authors claim to have described in the case of iron and steel, is due to the fact that the hydrated ferric oxide does not adhere to the surface of the metal, and that in consequence electro-chemical action can proceed freely without the interruption due to the introduction into the circuit of a large amount of resistance.

Influence of Motion of Sea Water.—In all the experiments hitherto described, the rate of complete corrosion has been very slow ; it follows, however, from the nature of the reaction as outlined above that if the sea water were kept continually in motion, as is the case in condensers, it would be considerably

accelerated. In stagnant sea water the layer in contact with the oxide film will quickly become impoverished in salt by reaction with the oxide, and fresh salt can only reach the tubes by the slow process of diffusion. Thus, it has been found, by daily weighing experiments conducted on tubes suspended in stagnant water, that the rate of corrosion is always much faster during the first day than afterwards. At first, the rate is determined by the speed of reaction between the oxide and the salt, but after the first few hours it is determined principally by the rate of diffusion of salt and oxygen, and since this is slow the speed of corrosion falls off considerably. Possibly the zinc passes rapidly into solution during the interval of time before the formation of the oxide layer. These points are illustrated by the curves shown in Figs. 8 and 9.

Curve 1 (Fig. 8) shows the results obtained from a continuous aeration experiment, in which two 70 : 30 tubes were immersed in $1\frac{1}{2}$ litre of sea water, through which air was kept continually bubbling, and thereby the speed of corrosion is almost doubled compared to the rate of corrosion in stagnant sea water, as represented by curves 2, 3, and 4.

The curves shown in Fig. 9 were obtained from the results of an experiment in which 4 litres of sea water were circulated continuously by means of a pump along two 6-inch lengths of 70 : 30 tube which had been cut in half along a diameter. Under these conditions the speed of corrosion is further increased to approximately four times the rate obtaining in stagnant sea water (an accurate comparison cannot be made, since only a portion of one side of the tubes was exposed to attack by the flowing current of sea water). A uniform tenacious oxide layer was formed on these tubes similar to that on the tubes immersed in stagnant sea water, but was somewhat darker in colour.

Further experiments were carried out with circulating sea water on the effect (if any) of particles on brass corrosion. Pieces of coal and clinker were tied on near the centre to 6-inch lengths of each of the four kinds of tube and sea water circulated along the tubes continuously for thirty days. On examination at the end of this time none of the tubes showed

any traces of localized corrosion in the neighbourhood of the particles. On the other hand, beneath the coal was found a bright unoxidized patch, confirming previous observations that such particles only exert a mechanical protective action.

Influence of Deposits of Basic Salts.—In view of the fact that neither copper nor carbon particles set up any electrolytic action when in contact with a tube, it seemed unlikely that

Comparison of Different Methods of Corroding.
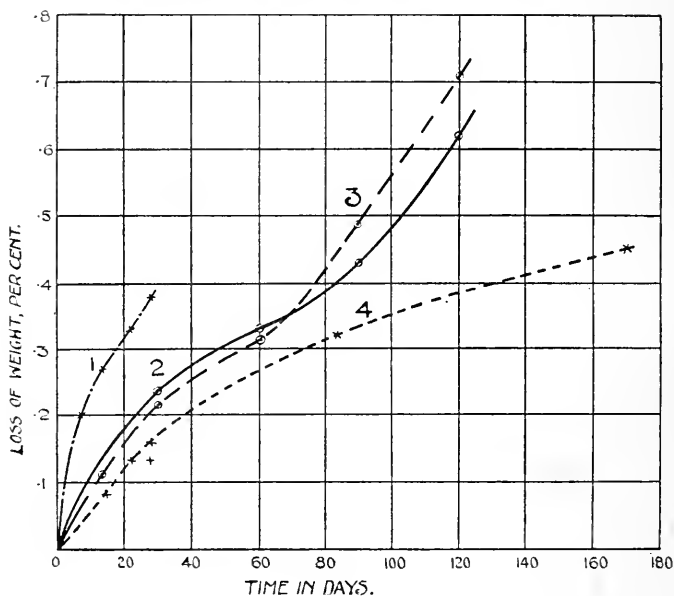
Fig. 8.

1. Continually aerated test in $1\frac{1}{2}$ litre sea water.
2. Horizontal immersion in $1\frac{1}{2}$ litre sea water.
3.   ,,   ,,   4 litres sea water.
4. Vertical   ,, $1\frac{1}{2}$ litre sea water.

such poor conductors of electricity as the green basic salts which are formed during corrosion would have any effect. There still remains the possibility that they might exert direct chemical or catalytic action.

In the horizontal immersion tests when the ordinary green deposit was allowed to settle on the tubes its influence was

shown to be very slight. In this case, however, the deposit never adhered tightly to the tube. In order to test whether it would exert a greater effect when it adhered firmly to a tube, a wet and dry test was carried out by immersing two tubes for one day in sea water, and allowing them to dry in air on the next, and so on alternately for sixty days.

The results showed an increased loss of weight as compared with the ordinary continuous immersion tests, but no signs of selective corrosion were observed. Hence it may be concluded

Tube X.   *Tube* Y.
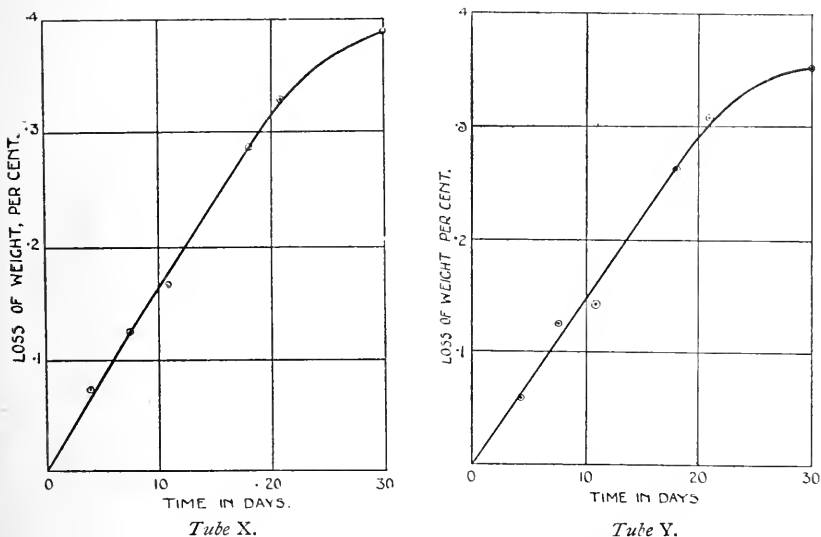
FIG. 9.—Results of Corrosion by Running Sea Water.

that at ordinary temperatures the greenish-blue deposit does not give rise to selective corrosion.

It has already been mentioned that a portion of the zinc which is removed from the tube in the course of the complete type of corrosion remains in solution as chloride. It is well known that this substance in aqueous solution has an acid reaction, owing to hydrolysis, thus—

$$ZnCl_2 + 2H_2O \rightleftarrows Zn(OH)_2 + 2HCl.$$
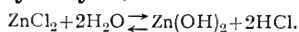
On concentration of the aqueous solution—

$$ZnCl_2 + H_2O \rightleftarrows HCl + Zn(OH)Cl$$
$$2Zn(OH)Cl \rightarrow Zn_2OCl_2 + H_2O$$
(insoluble white basic chloride).
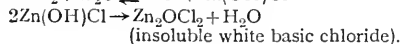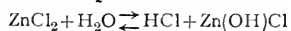
Experiments have repeatedly shown that if hydrochloric acid, even when dilute, be allowed to evaporate in contact with a piece of $70:30$ brass tube, a green basic chloride is formed, and superficial dezincification, *i.e.* selective corrosion, takes place, leaving a copper-rich layer.   It was thought, therefore, that zinc chloride would act in the same way by generating hydrochloric acid as indicated by the reactions given above.   Moreover, the production of hydrochloric acid, if it occurred, would be regenerative, as shown by the equation given above.

The following experiments were therefore tried :—

1. Moist zinc chloride was left in contact with a tube for some days at the ordinary temperature.   No dezincification was observable.

2. Moist zinc chloride was next placed inside a tube, and the whole heated to $70-80°$ C.   Pronounced dezincification was observable wherever the moist salt had been in contact with the metal.

3. Zinc chloride was placed upon a tube suspended in ordinary sea water.   No selective corrosion occurred, but the tube did not oxidize, retaining its yellowish colour as if protected from corrosion.

It is evident, therefore, that zinc chloride, if it can accumulate at any point on a tube, might start dezincification if the condenser tubes were hot.   It is not, however, very easy to see in what way this salt can accumulate at any one definite spot.   The most probable way seems to be as follows :—Drops of concentrated water might form many times in a certain definite position on a tube when the condenser was emptied, these might finally dry up and give rise each time to a considerable amount of basic salt which might be rich in zinc chloride.   In the presence of fresh supplies of moisture the chloride might be hydrolyzed and give rise to dezincification.

Accordingly the following experiments were tried :—

Drops of sea water were placed on three tubes and allowed to evaporate completely.   As soon as this occurred the drops were renewed, and in this way a quantity of basic salt was accumulated at certain points on the tubes.   One of the tubes was then heated to $55°$ C., another to $100°$ C., and a

third was not heated at all. The deposits on the three tubes would thus represent three states of basicity—that heated to 100° C. being the most basic. Next, they were all immersed in sea water for four weeks. Corrosion of the complete type increased with the degree of the basicity of the salt, but no dezincification or selective corrosion was observable.

A number of other similar experiments with various deposits of basic salts were tried. In some cases these appeared to have some slight influence on the rate of complete corrosion, but in no case was the influence sufficient to exert any appreciable effect on the life of the tube.

Experiments with Jelly Indicator.

It was thought that some light might be thrown on the phenomena of dezincification by the use of a test similar to that used by Walker and others for studying the corrosion of iron and steel, and called by them the ferroxyl test.

The test was originally devised for the purpose of ascertaining at what particular area on a sample of metal iron passed into solution with the formation of rust. The test was carried out in exactly the same manner as for iron and steel, except that potassium ferrocyanide was substituted for potassium ferricyanide, since the former gives an easily recognizable white precipitate with zinc, and a brownish-red precipitate with copper.

Experiments were carried out with jellies made up with distilled water and sea water. Ordinary pieces of 70 : 30 tube, when tested in these jellies, showed no well-defined local action. In both cases the jellies showed metal passing uniformly into solution with production of a pink phenolphthalein colouration all over and around the tubes. After immersion in the jelly for a few days the tubes became covered with a slimy brown layer of the precipitated metallic ferrocyanides.

General Conclusions to be drawn from the Experiments at Atmospheric Temperature.

1. Corrosion at this temperature in ordinary sea water is

D

always of the complete type and is very slow, and further it decreases in rate with progress of time.

2. Particles such as carbon in the form of coke, coal or graphite, sand, &c., have little or no effect on the speed or type of corrosion.

3. The greenish-blue deposit formed during corrosion has very little effect on the speed of corrosion.   Ferric oxide appears to exert some slight accelerating effect, but it is too small to be practically important.

4. The alteration in the concentration of the sea water affects the speed of corrosion as follows :—An increase of concentration increases the speed ; a decrease of concentration (or dilution of the sea water) decreases the speed, and to some extent alters the type of corrosion after a long period of immersion.

5. No evidence is forthcoming that " flaws " and " spills " have any influence on corrosion at ordinary temperatures.

6. The rate of corrosion is approximately the same in the case of $70:30$ brass and the $70:28:2$ alloy.   The rate of corrosion of Muntz metal is slower, and that of the $70:29:1$ alloy is faster than that of the other alloys.

7. The order of resistance to selective corrosion, induced by diluted sea water, showed the $70:28:2$ brass to be the most resistant (to date has resisted completely), and Muntz metal the least resistant.

8. Free hydrochloric acid will give rise to corrosion of the selective type at the ordinary temperature, but is either not formed at all from zinc chloride in the presence of sea water, or is formed in too small a quantity to be harmful.

EXPERIMENTS CARRIED OUT AT 40° C.

For these experiments a large gas-heated thermostat, which would hold sixteen beakers, was fitted up.   In each beaker were placed $1\frac{1}{2}$ litre of sea water, and they were suspended in the thermostat by means of wooden trays.   The surface of the water in the beakers was left open to the air, and evaporation was made good each day by means of distilled water.   The water sur-

rounding the beakers in the thermostat itself was covered with a layer of liquid vaseline to diminish evaporation. The temperature of the thermostat remained constant to within a quarter of a degree, and this was sufficiently accurate for the purpose in view. A pair of 3-inch lengths of each of the four standard tubes were immersed in four of the beakers, in a precisely similar manner to that described in the horizontal immersion tests. The thermostat was heated continually night and day and throughout the week ends.

The first stage of corrosion appeared to be identical with that which occurs at the ordinary temperature, viz.: oxidation of the surface of the tubes, but the layer of oxide was formed more rapidly; Muntz metal must be excepted from this statement, since the metal appeared quite bright and unoxidized. The second stage of the process was the formation of an insoluble green deposit which contained both copper and zinc, and closely resembled that formed at the ordinary temperature. As before, part of the zinc remained in solution. The tubes were removed and weighed every week, and the results are shown in Table VIII., and are plotted in the curves shown in Fig. 10. It will be seen that the order in which the tubes resist corrosion at 40° C. differs from that at atmospheric temperature.

In a number of the experiments at 40° C. dezincification was observed. Whenever this occurred a white salt was formed in addition to the greenish-blue salt already described. The white salt was found to be oxychloride of zinc, and it adhered firmly to the tubes in spots. In consequence of this, the losses of weight in these experiments are not so reliable a measure of the amount of corrosion as in the experiments conducted at the ordinary temperature.

The first tubes to show signs of dezincification were those of Muntz metal. An adherent white deposit, sticking to the tube in small patches at the edges and at the ends, was clearly visible at the end of seven days. Beneath each white speck a small dezincified area was found. The rest of the tube retained its bright appearance. The dezincified spots increased in number as time went on, and at the end of a month the greater part of the edges and ends of the tube

TABLE VIII.—*Tests at* 40° C.

	Interval	1. 70:30 A	B	2. 70:28:2 A	B	3. 61:39 A	B	4. 70:29:1 A	B
Initial weight in grammes	…	19·0271	20·7267	22·3552	22·6423	21·0340	21·8345	19·1612	18·7671
Weight after .	7 days	19·0010	20·7050	22·3306	22·6156	21·0277	21·8293	19·1454	18·6890
Loss in weight	…	0·0261	0·0217	0·0246	0·0270	0·0063	0·0052	0·0158	0·0181
Percentage loss	…	0·13	0·11	0·11	0·12	0·03	0·025	0·08	0·09
Weight after .	14 days	18·9928	20·6882	22·3185	22·6023	21·0270	21·8275	19·1432	18·6873
Percentage loss	…	0·18	0·14	0·16	0·19	0·035	0·03	0·09	0·10
Weight after .	28 days	18·9860	20·6885	22·3040	22·5830	21·0145	21·8130	19·1380	18·6840
Percentage loss	Sea water renewed	0·21	0·19	0·23	0·26	0·095	0·10	0·12	0·12
Weight after .	35 days	18·9815	20·6830	22·2985	22·5710	21·0115	21·8105	19·1340	18·6819
Percentage loss	…	0·24	0·21	0·28	0·31	0·11	0·11	0·14	0·14

were coppery in appearance.   Dezincification had also begun on the backs of the tubes.
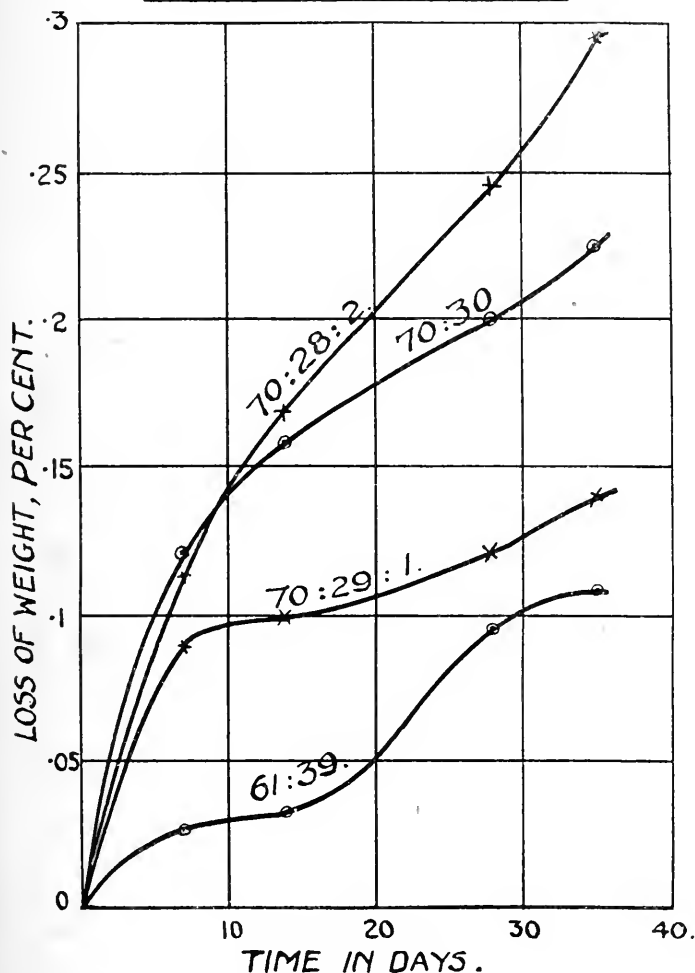
FIG. 10.—Corrosion at 40° C.

The next to show dezincification was the 70 : 30 brass. It was noticed on one of the two tubes at the end of a fortnight, but the other was apparently not affected.   At the end

of a month, however, dezincification was quite marked along the edges and ends of both tubes and on the back of one only.

The $70 : 29 : 1$ tubes showed slight traces of dezincification at the end of three weeks. In the case of these tubes it occurred on the interior surfaces near the end.

The $70 : 28 : 2$ tubes appeared to be the most resistant to selective corrosion. At the end of a month there were but very slight traces of dezincification along the sides of the interior surfaces of the tubes.

A considerable number of other experiments were carried out at $40°$ C. on $70 : 30$ brass tubes. It was observed that in the great majority of cases dezincification began along the sawn edges of the tubes. Two explanations of this observation suggested themselves. In the first place, it was just at these edges that diffusion, both of oxygen and salt, took place most rapidly, and this fact alone might be sufficient to account for the increased action in that position. An alternative view was that these edges, which had been sawn and only roughly smoothed, afforded better loci for the deposition of the white basic salt, which in some way facilitated the attack on the zinc of the brass.

To test the latter view, two tubes were polished all over very carefully so that the physical condition of the edges and ends was as nearly as possible identical with that of the inner surface. These tubes were then placed in a beaker in the thermostat along with the other tests. At the end of a month it was found that one of the tubes showed severe dezincification along one edge only, while the other tube was dezincified only along the bottom edge of the inner surface, and not at all along the edges. The result is not entirely conclusive, but, taken in conjunction with the results obtained with other tubes, appears to point to the fact that the physical condition of the surface exerts some influence in determining the areas at which dezincification appears.

Influence of Concentration of Sea Water at $40°$ *C.*—The samples of the sea water used in this section of the work were of concentration $0·5$ (diluted sea water) and 2.

In the case of the diluted sea-water both tubes clearly showed dezincification at the end of seven days, and at the

end of one month it had become fairly general all over the tubes; patches of the white basic salt were widely distributed. In the case of the concentrated sea water, the tubes at the end of a fortnight exhibited a light yellowish-brown oxidized appearance ; no particles of white salt adhered to the tubes, nor was any sign of dezincification visible on either tube. After a period of one month white spots began to appear, showing that concentrated sea water has a retarding, but not preventative, effect on the occurrence of selective corrosion.

Influence of Substances in Contact with Tubes at 40° *C.*

(A) *Graphite on* 70 : 30 *Tubes.*—After twenty-eight days the tube was bright and unattacked beneath the graphite. At the edges of the graphite, layers of bluish and reddish oxide were visible. These were evidently due to the mechanical prevention of diffusion by the graphite, whereby the salt was unable to attack the oxide. The tubes showed dezincification in spots, mainly along the edges as in the case of the bare tubes discussed above. The locality of the spots showed no definite relation to the position of the graphite.

Graphite on 70 : 29 : 1 *Tubes.*—The appearances presented by these were similar to those of the 70 : 30 tubes, except that no dezincification was observable.

(B) *Copper Plug Experiment.*—A 70 : 30 tube with a copper plug screwed into it was placed in a beaker with a check tube ; at the end of a month both tubes exhibited general dezincification at the edges. The metal in the neighbourhood of the copper plug was not specially attacked. The presence of the copper plug evidently had no effect on the distribution of the areas of selective corrosion. The plug itself was covered with a layer of cuprous oxide.

(C) *Precipitated Zinc Hydroxide.*—It was thought that a slow inter-action might take place between this substance and the salt in sea water and give rise to the oxychloride, which is formed as a result of selective corrosion and which appears to have an accelerating, or at least localizing, effect upon the reaction. Accordingly a check tube and a tube upon which zinc hydroxide had been placed were exposed to

the action of sea water for a month at 40° C. A slight dezincifying action was observed beneath the hydroxide deposit, and it seemed probable that the expected reaction took place to some extent, but was slow and required a considerable time to become effective.

(D) *Ferric Oxide.*—This substance seemed to have a slightly accelerating effect on the rate of complete corrosion, as noticed previously for corrosion at atmospheric temperature. It did not appear to increase selective corrosion.

(E) *Zinc Chloride.*—This substance when brought into contact with sea water formed a highly insoluble finely divided oxychloride which settled on the tubes, and set up active dezincification. The action was most intense at the edges, which became uniformly coppery in colour. No complete corrosion took place—the tubes retaining their bright yellow colour, and their loss in weight was much smaller than in the normal case.

Consideration of the Results of Experiments at 40° C.

One fact of predominating importance has been brought out by these experiments, viz. that brass tubes of any of the standard compositions will become dezincified by the action of sea water at this temperature. The order of resistance to this type of corrosion is:

      (1) Muntz metal (the least resistant).
      (2) 70 : 30 brass.
      (3) 70 : 29 : 1.
      (4) 70 : 28 : 2.

Dilution of the sea water increases the tendency towards selective corrosion; concentration of the sea water tends to repress it.

The effect of particles was unimportant, with the exception of zinc oxychloride and possibly zinc hydroxide.

The position at which dezincification began was determined largely by the physical condition of the metal and by the points to which diffusion could take place most rapidly, and not by the electro-chemical effect of particles.

In no case were the tubes dezincified to any great depth by

immersion for one month, and the experiments must be continued for a much longer period before a quantitative expression can be obtained for the rate of progress of dezincification through the tube.

Although at $40°$ C. the type of corrosion is selective to some extent, yet it is not entirely concentrated upon the zinc. In all cases a certain amount of loosely adherent greenish-blue salt was formed, which closely resembled that observed at the ordinary temperature. The formation of this salt did not appear to be confined to definite parts of the tube, but to take place generally, except just at those points where dezincification was in progress. On the other hand, dezincification began at certain definite spots and spread gradually. At these spots white basic chloride of zinc was formed and adhered firmly to the tubes. The nature of the action seems to the authors to be as follows:—

At $40°$ C. the normal action of sea water is slight preferential solution of the zinc, but some copper is removed from the metal at the same time. The zinc chloride, which rapidly accumulates in the solution, reacts with oxygen to form a basic oxychloride, which is precipitated upon the tube at any point of roughness, or on any particles of foreign matter which themselves stick to, or slightly roughen, the tube, and so present nuclei for the precipitation of the salt. When once this white salt has been deposited at any point the action becomes localized, and it seems as if the salt has a regenerative action in bringing about the transfer of chlorine from the sea water to the zinc of the brass.

It is now abundantly evident that temperature is a factor of prime importance in determining the type of corrosion of brass. Even at $25°$ C., that is, at only a slight elevation above the ordinary temperature, it has been found that selective corrosion of $70:30$ brass becomes visible after a few weeks' immersion in sea water. It is a remarkable fact that Bruhl [*] mentions the results of two loss-of-weight experiments carried out at $40°$ C. for nine weeks with $70:30$ brass, but gives no details of the appearance of the tubes, and makes no mention of dezincification, nor does he refer to any difficulty

* *Loc. cit.,* p. 289.

met with in removing oxychlorides.   No analysis or description of the brass used, or details of the method of experiment, are given in his paper, but the metal appears to have been brass plate.   The present authors have observed dezincification at 40° C. in twenty different samples of tube, and only one sample successfully resisted it for a month.   It should perhaps be mentioned that Bruhl used synthetic sea water, whereas the authors used natural sea water.

Relation between Loss of Weight and the Occurrence of Dezincification.

An examination of the tables and curves on pp. 35, 36 and 52, 53 will show that the loss of weight for a given time of immersion in the case of 61 : 39 and 70 : 28 : 2 alloys is slightly greater at 40° than at the ordinary temperature, while in the case of 70 : 30 alloy it is about the same, but much smaller for Admiralty metal, so that the relative order in which the tubes lose weight differs from the order at the ordinary temperature (see p. 50).   Moreover, there is no definite relationship between the total loss of weight and the resistance to dezincification.   Thus Muntz metal, which loses least in weight, is most readily dezincified ; as regards loss of weight it is followed by the 70 : 28 : 2 alloy, but the 70 : 30 brass is the next most easily dezincified tube.

It should be borne in mind that in all cases in which dezincification takes place, the loss of weight results are less accurate than when no such action takes place.

It is, however, quite evident that loss-of-weight experiments conducted at the ordinary temperature for periods of a few months only, give no clue whatever to the behaviour of the alloys at 40° C. as regards dezincification.

The small losses of weight shown by Muntz metal after dezincification has begun are due mainly to the fact that though dezincification begins soon and penetrates deeply, yet it is severely localized.

EXPERIMENTS CARRIED OUT AT 50° C.

Observations made upon the temperature of the outlet water from condensers in practical use showed clearly that much higher temperatures than 40° C. occurred frequently in the interior of the condensers. It is not very unusual for the outlet water to reach a temperature of 45° C., especially in the case of ships trading in the tropics, and this indicates that at certain points along the interior of the tubes the temperature of the water would be at least 50° C. In view of the results obtained at 40° C., it therefore appeared desirable to examine the effects produced during corrosion at a higher temperature.

Accordingly, an electrically heated thermostat was installed to run at 50° C. Beakers of sea water were suspended in the thermostat by means of wooden trays and a pair of 3-inch tube lengths immersed horizontally in each beaker as before.

The experiments at 50° C. were confined mainly to the 70 : 30 and 70 : 29 : 1 alloys, as the space in the apparatus was more limited than in the case of the thermostat at 40° C.

The 70 : 30 tubes showed clear signs of dezincification after seven days' immersion ; the action began at the edges and ends, and spread later to the backs and interior surfaces of the tubes.

The 70 : 29 : 1 tubes were far more resistant than the 70 : 30, and no signs of dezincification could be detected at the end of six weeks' immersion. In view of the fact that this alloy showed slight dezincification at the end of three weeks at 40° C. this result is remarkable, and it appears to indicate that there is a limited range of temperature over which dezincification can take place. The matter deserves further investigation.

The layer of oxide formed at this temperature was less uniform than usual and decidedly darker in colour than that formed at the lower temperatures. Wherever free access of oxygen was limited by the presence of string, coal, or other substances in contact with the tube a bright red form of cuprous oxide was noticeable, especially in the case of the 70 : 29 : 1 alloy.

The deposit formed as a result of the corrosion of the 70 : 30

tubes was in all cases of a dirty white colour, very different from the green-blue basic salt formed at lower temperatures. It was found to contain only traces of copper, and consisted almost entirely of basic chloride and carbonate of zinc. The deposit formed from the $70:29:1$ tubes was of a pale green colour, lighter than that obtained at the ordinary temperature.

It will now be realized that the effect of temperature is of predominating importance in determining the nature of the reaction which takes place when brass is corroded by sea water.

At the ordinary temperature both copper and zinc are removed from the metal, approximately in the proportions in which they are present in the brass; and that uniformly over the whole surface of the metal. As the temperature is raised less and less copper is removed proportionately to the zinc, and at a temperature of $50°$ C. the attack is concentrated almost entirely on the zinc.

The presence of tin in the brass exerts a powerful effect in retarding selective corrosion, as described above. The way in which it exerts this effect is not yet clear, and should be the subject of further investigation.

It will be noticed from the curves on page 62 that the total loss of weight of $70:30$ brass at $50°$ C. is rather smaller than at the ordinary temperature for an equal period of time.

It seemed probable that this was due to the decreased solubility of oxygen at the higher temperature. In order to test this a $70:30$ and a $70:29:1$ tube were immersed side by side in a beaker into which air was pumped continually by a motor-driven force pump, so that the sea water in the beaker was kept continually in a state of violent agitation.

This experiment seemed to the authors particularly important from an entirely different point of view, since it would afford evidence of the effect of the motion of the sea water upon the adherence of the oxychloride to the tube.

The results of the experiments as regards loss of weight are given in Table IX. and Fig. 11. It will be seen that the speed of corrosion is enhanced by the aeration of the water, and is much in excess of that at the lower temperatures.

Moreover, these experiments brought to light the important fact that agitation of the water does not prevent the sticking of the oxychloride to the surface of the tube; rather the selective corrosion seemed to be increased under these con-

TABLE IX.—*Tests at* 50° C.

| | Interval. | Continually Aerated. | | Not Aerated. |
		1. 70 : 30	4. 70 : 29 : 1	1. 70 : 30
Initial weight in grammes . .	...	21·8007	18·1943	20·9700
Weight after	7 days	21·7630	18·1810	20·9562
Loss in grammes . . .	...	0·0377	0·0133	0·0138
Percentage loss	...	0·17	0·07	0·07
Weight after	14 days	21·7446	18·1740	20·9508
Percentage loss	...	0·23	0·11	0·09
Weight after	21 days	21·7346	18·1680	20·9390
Percentage loss	Sea water renewed	0·30	0·145	0·15
Weight after	28 days	21·7182	18·1600	...
Percentage loss	...	0·38	0·19	...
Weight after	35 days	21·7070	...	...
Percentage loss	...	0·43	...	...
Weight after	42 days	21·7000	...	...
Percentage loss	Sea water renewed	0·46	...	...
Weight after	49 days	21·6965	...	...
Percentage loss	...	0·48	...	...

ditions, and this observation agrees well with the evidence obtained from tubes corroded in practice, in which the oxy-chloride was found to adhere tightly to the tubes, in spite of the fact that the water is circulated rapidly through them.

Effect of the Concentration of the Sea Water at 50° *C.*

The effect of the concentration of the water at this temperature was only studied for the cases of sea water of concentrations 0·5 and 4. In the former case dezincification of a 70 : 30 tube became evident at the edges and over the whole surface after immersion for six or seven days.

In the case of the concentrated sea water, selective corrosion, though not altogether prevented, was distinctly repressed;

the deposit obtained in this experiment was of a pronounced green colour, showing that complete corrosion had taken place to some extent.

EXPERIMENTS AT 50°C.
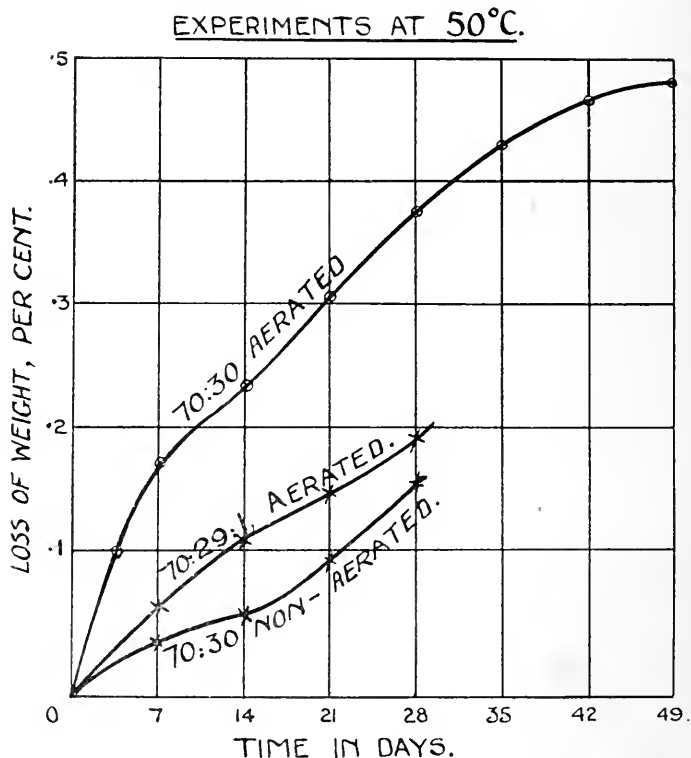
Fig. 11.

EFFECT OF PARTICLES AT 50° C.

The effect of coal upon $70:30$ and $70:29:1$ tubes was observed for six weeks, the sea water being aerated continuously throughout this time, as described above. The $70:29:1$ tubes showed no sign of dezincification at the end of this time; but the $70:30$ tube showed the usual amount characteristic of the alloy for this period of time. The coal exerted no special effect upon the tubes other than one of mechanical interference with diffusion.

Ferric oxide did not cause dezincification of a $70 : 29 : 1$ tube in twenty-one days, but appeared to increase slightly the dezincification of $70 : 30$ brass by affording loci for the deposition of oxychloride. The effect of graphite and of zinc chloride was similar to that which had been observed at a temperature of $40°$ C.

The effects of magnesium hydroxide and chloride were also observed, but were found to have no special effect on the type or extent of corrosion.

SECTION II.

The Experimental Condenser Plant.

In the laboratory experiments hitherto described the principal object kept in view was the investigation of the separate effect of each of a number of the conditions to which a tube might be expected to be subjected in the condenser. In some cases the simultaneous effect of two influences was investigated, as, for instance, those of temperature and deposits, but for the most part the conditions were kept simple.

It seemed very desirable, however, to observe the joint effect of all the influences to which a condenser tube might be subjected under the simplest possible conditions of practice, and to arrange matters in such a way that the nature of these conditions could be ascertained as accurately as possible. It was thought that, with the knowledge of the effect of each condition separately obtained in the laboratory, it might be possible to interpret the results obtained in the more complicated case.

Accordingly, it was decided to erect an experimental plant, which should subject forty-eight condenser tubes to conditions approximating, as nearly as possible, to those obtaining in the ordinary practice of the mercantile marine.

Description of Plant.—The general nature of the required plant was arranged by one of the authors, with the aid of the members of the Corrosion Committee. The engineering

details were worked out, and the plant was supplied and erected by Mr. W. W. Strafford of Great Crosby, Liverpool, and has fulfilled its purpose satisfactorily.

An elevation of the plant is shown in Fig. 12. A is a tubular boiler of special design, which worked under normal conditions at a steam pressure of 125 lb. per square inch. The steam passes through the pressure-gauge and throttle shown to the pipe B, and then to the dual expansion engine C. From the low-pressure cylinder of the engine the exhaust steam passes along pipe D to the four steel cylinders marked E. Each of these cylinders constitutes a separate condenser holding twelve tubes, each 3 feet long. One of these cylinders is shown separately in Fig. 13. The steam from D passes through the control cocks D′ (Fig. 13) into the space surrounding the tubes, which are arranged as shown in the elevation of the tube-plate in the lower part of the figure.

After the condensation of the steam, the resulting water leaves the condensers by the pipes F and G, and passes through air pump H, which is hardly visible in the drawing, and reaches the hot-well I. From this it was originally picked up by the pump K and returned to the boiler through pipe L and an injector. Later, since oil accumulated in the hot-well to some extent, and consequently corrosion of the boiler was feared, the hot water in I was thrown away and a separate container I′ was used to supply clean water to the boiler.

The circulation of the sea water through the tubes was carried out as follows :—A steel tank, which would hold about 600 gallons of sea water, was fixed in the open air outside the building which held the rest of the plant. It was protected from rain, &c., by a cover of galvanized iron raised about a foot above the top of the tank on iron supports ; the intervening space was covered in by wire netting. Thus air had free access to the tank, but wind-borne rubbish was excluded. The inside surface of the tank was protected by a thin wash of cement.

The sea water from the tank passed by gravity through iron pipes about 50 feet long into the room containing the condenser, where it reached the pipes L and M. From these four side tubes M′ led into the four cast iron water ends, X,
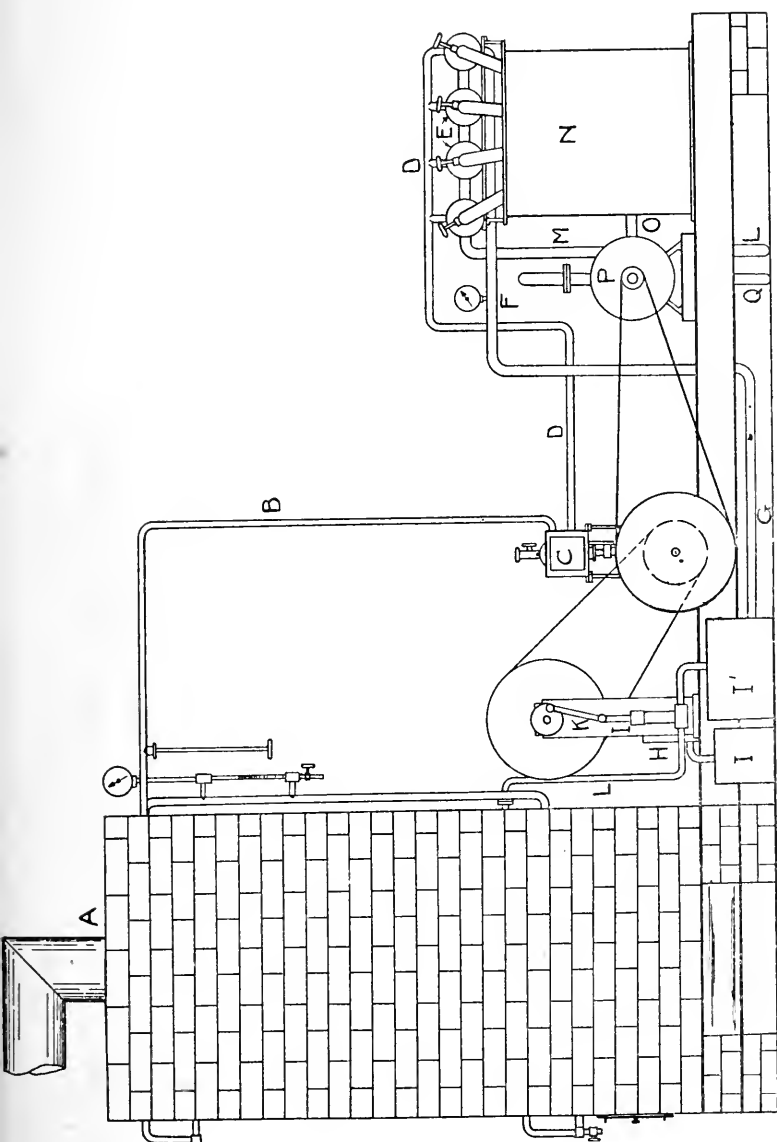
Fig. 12.—Elevation of Plant.
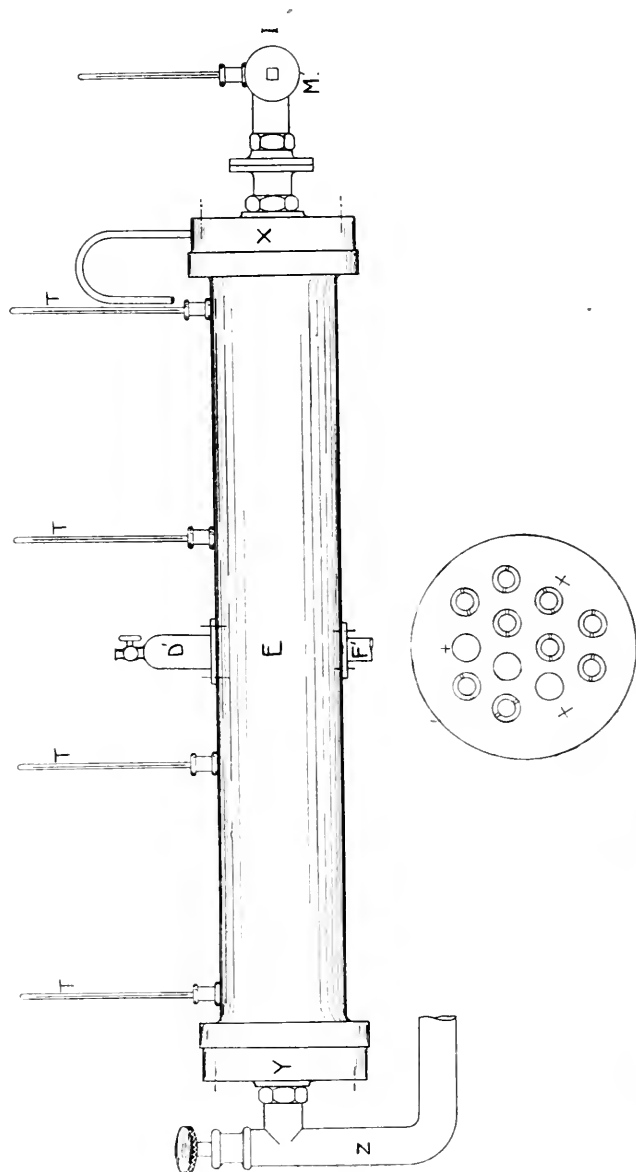
Fig. 13.—Diagram of Condenser Cylinder.

of the condensers. It then passed through the tubes and out into the water spaces, Y, at the far ends of the condensers, and so by pipe Z into the tank N. From this it was collected by the centrifugal pump P, and sent back through pipe Q to the large outside tank. To reach this it had to pass through 50 feet of iron tubing, and was afterwards delivered in a shower at a distance of some 3 feet above the level of the water in the tank. Consequently, the water which had been heated by its passage through the condensers was cooled considerably before passing again through the tubes.

Composition of the Condenser Tubes.—Four standard types of tube were selected by the Corrosion Committee as being most suitable for detailed examination. Their compositions were as follows :—

	1. 70 : 30 Brass.	2. 70 : 28 : 2(Pb) Special Brass.	3. 61 : 39 Muntz Metal.	4. 70 : 29 : 1 Admiralty Brass.
Copper	70·21	69·94	60·90	71·18
Zinc	29·17	27·60	38·21	27·28
Tin	...	...	...	1·07
Lead	0·27	2·08	0·46	0·28
Iron	0·27	0·28	0·33	0·21
	99·92	99·90	99·90	100·02

The tubes of the first three types were kindly presented to the Committee by Messrs. Muntz's Metal Company, Ltd., of French Walls, Birmingham, and the tubes of type 4 by Messrs. The Broughton Copper Company, Ltd., of Manchester. The latter firm also presented an additional quantity of 70 : 30 brass,which was required for the laboratory work. The authors tender their grateful thanks to both these firms.*

Composition of the Sea Water.—The sea water used in the experiment was taken at high tide from deep water at Formby, at a point well outside the mouth of the river Mersey. The composition of the sea water was as follows :—

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* It should be mentioned that no difference whatever could be detected in the behaviour of the 70 : 30 tubes made by these two firms, though they were used side by side in a number of the laboratory experiments.

						Per Cent.	
Sodium chloride	.	.	.	.	.	2·81	⎱ Total chloride
Magnesium chloride	.	.	.	.	.	0·21	⎰ 3·19 per cent.
Potassium chloride	.	.	.	.	.	0·17	
Magnesium sulphate	.	.	.	.	.	0·11	
Calcium sulphate	.	.	.	.	.	0·08	
Calcium carbonate	.	.	.	.	.	0·02	

Specific gravity at 17·6° C. = 1·0225.

Owing to the expense of carting large quantities of sea water, it was desirable to use the same sample for as long as possible. Accordingly, the specific gravity and the chlorine
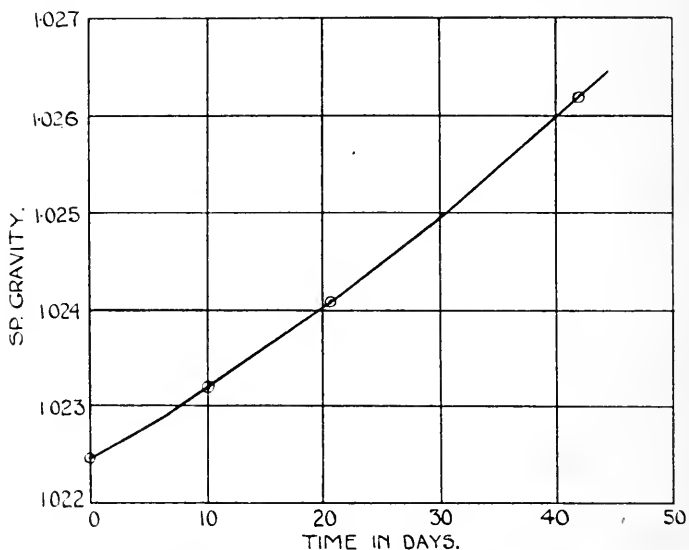
FIG. 14.—Change in Specific Gravity of Sea Water.

content of the water were estimated weekly, so as to afford a guide as to the alteration of the composition of the water with time. Owing to loss by evaporation, both the specific gravity and total chlorine increased slowly in a manner shown by the curves traced in Figs. 14 and 15. It was decided that the total chlorides should not be allowed to exceed 4 per cent.,* and accordingly it became necessary to change the water every six weeks in warm weather. Rather longer runs were possible in cooler months.

* Laboratory experiments described previously show that a small increase in concentration does not affect the speed of corrosion appreciably.

Sea water was circulated through the tubes every day for nine hours, at the end of which time the steam and water were cut off and the plant was allowed to cool down. It would have been advantageous to circulate the sea water continuously night and day, but the funds available did not permit of the payment of an attendant for the night shift. When the supply of water from the main tank to the condensers was cut off—as, for instance, at night and on Sundays—a small amount of water always remained at the bottom of the tubes. The plant was run for half a day on Saturdays
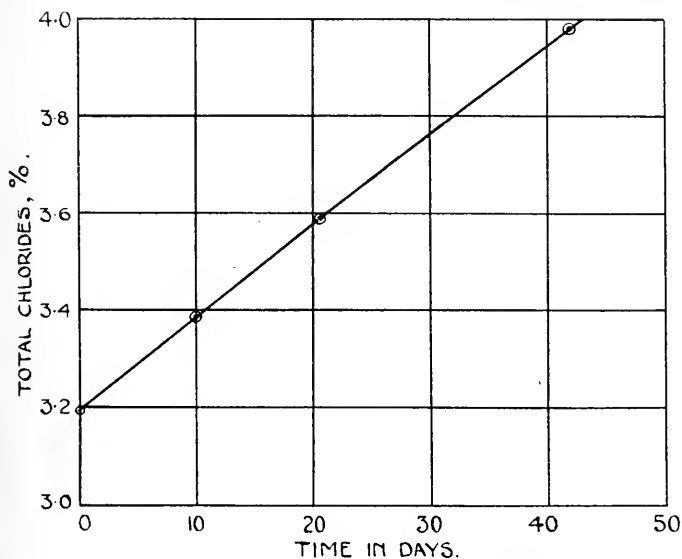
Fig. 15.—Change in Chlorine Content of Sea Water.

and remained idle all Sundays. The total period during which the plant was run in the manner indicated was nine months, at the end of which time it became necessary to close it down owing to lack of funds.

Temperature Conditions in the Plant.—The temperature of the inlet water rose gradually during each nine-hour period of running, especially in hot weather. It appeared to attain a maximum in about seven hours. The hottest weather during the period of the run occurred in May 1912, and a curve is plotted in Fig. 16 showing the rise in tempera-

ture during the day. The use of a much larger volume of water would have prevented, to some extent, this rise in temperature, but the additional cost of haulage would have been considerable. Moreover, it was only during the hot weather that the effect became important, and even in this case the conditions approximated to those which might arise on board a ship trading to the tropics.

It seemed desirable to obtain a knowledge of the temperatures obtaining in the interior of the condenser, since these could not be deduced from measurements made on the ingoing and out-going water. Accordingly, four thermometers
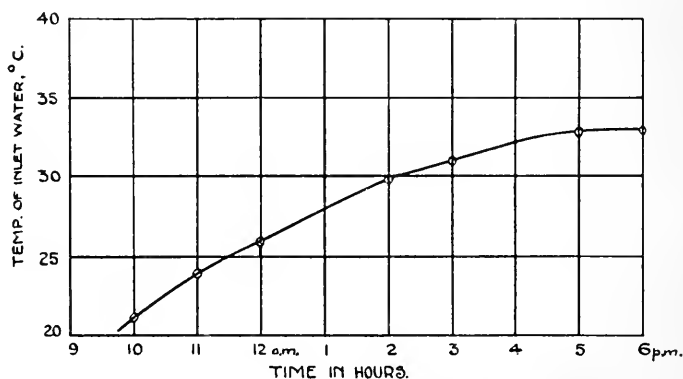
FIG. 16.—Rise in Temperature of Sea Water during Day.

were inserted through the casing of each of the four sections of the condenser in such a way that the bulbs of the thermometers were in actual contact with the top tubes. The thermometers were fixed in glands which were made perfectly steam-tight. The arrangement is shown at T in Fig. 13 (p. 66).

These thermometers served two purposes, viz. :—

1. That of enabling four sections of the condenser to be kept at approximately the same temperature by the adjustment of the amount of steam admitted to each.

2. That of indicating the distribution of temperature along each tube.

The actual temperatures observed depended principally upon four factors—(*a*) the atmospheric temperature, (*b*) the

amount of steam being condensed, (c) the time the plant had been at work, (d) the speed of the water through the tubes.

The factor (d) was kept constant throughout the whole of the experiments described in this paper, and its effect will not be considered further.

As regards factor (a) the plant ran from March 1912 till the following December, and during this period some of the highest temperatures recorded for the inlet water were obtained during the month of May. No severe frosts occurred during the whole run of the plant, and the lowest temperatures were observed during November. Typical curves illustrating the distribution of temperature along the tubes during May and November are shown in Figs. 17, 17a, and 18 (pp. 72, 73, and 74).

It was not found possible to separate the factors (a) and (b) from one another entirely, so that the actual temperature of the inlet water, after the run had once begun, depended on both factors jointly. The extremes in steam pressure recorded were 90 lb. per square inch and 135 lb., but for the most part the steam was kept in the neighbourhood of 125 lb.

An examination of the curves shown in Figs. 17, 17a, and 18 will show that the tubes in the four sections of the condenser had been subjected to temperature conditions that are nearly identical. Although the amount of steam admitted to each section could be controlled by a separate cock, it was not found possible to obtain greater equality of temperature than that shown in the curves. Sometimes one section was slightly the hottest and sometimes another, and the small differences appeared to be fairly uniformly distributed between the four sections. Difficulties in obtaining exact uniformity of conditions rapidly increase with the scale of the plant, and although the engine and pump were kept working as regularly as possible, it is to the unavoidable variations in these matters that the differences in temperature are due.

It may be mentioned that it was found difficult to keep the vacuum in the condenser above 20 inches, although occasionally it reached 25 to 27 inches. In ordinary mercantile marine practice the vacuum approximates more nearly to the higher figures.
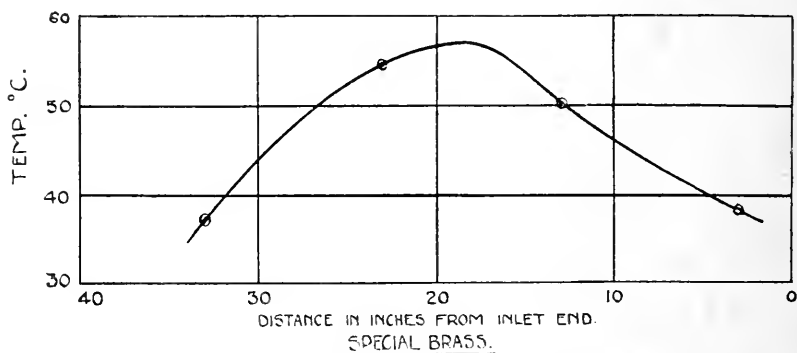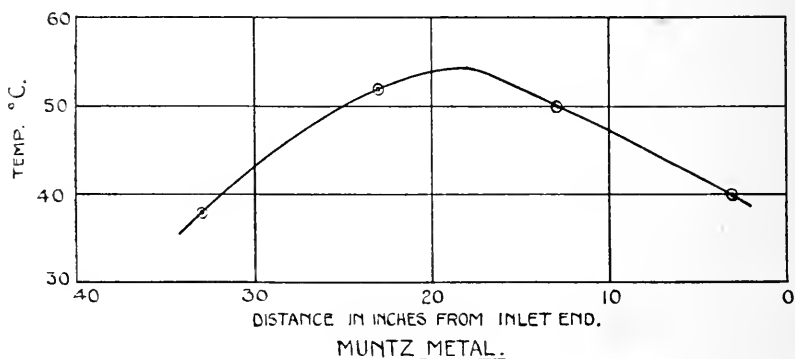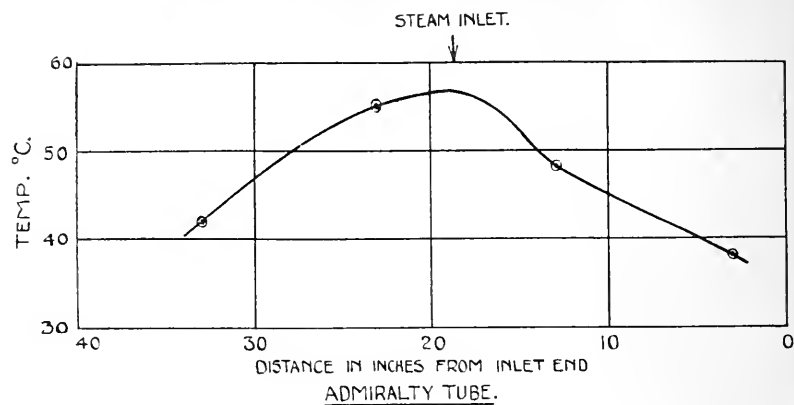
FIG. 17.—Temperature Distribution along Tubes in May.

The amount of steam condensed per hour per square foot of condenser surface was approximately 5 lb. This amount is also somewhat smaller than the normal practice in the passenger services, though it corresponds approximately with the amount condensed in cargo boats.

On the whole it is claimed that the conditions obtained in the mercantile marine have been reproduced as accurately as is possible on a small scale plant, and, at any rate, sufficiently accurately to yield valuable experimental results.

At the end of nine months' working the plant was closed down, and three tubes of each composition were removed for examination. They were selected from similar positions in
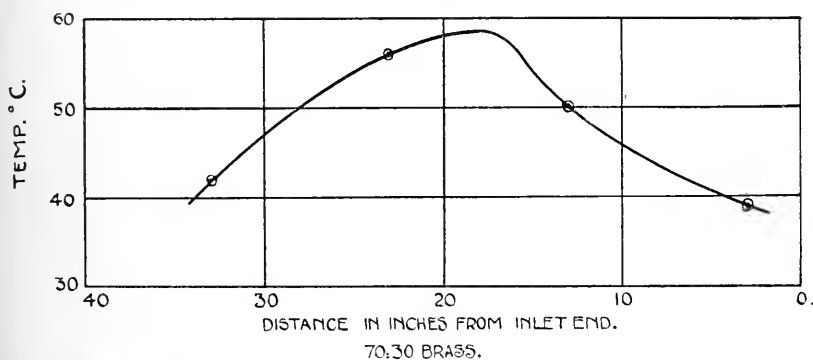
FIG. 17A.—Temperature Distribution along Tubes in May.

each of the four sections of the condenser, and the positions are indicated in Fig. 13, where the three blank spaces in the lower part of the figure indicate the positions from which the tubes were withdrawn.

After removal, the tubes were cut in half longitudinally, so that the interior surfaces might be examined.

Nature of the Scale.—In all cases the tubes were covered with a brown layer, which consisted chiefly of ferric oxide; it contained also sodium chloride and calcium carbonate, as well as traces of sulphate. This layer was loose and easily removed from the tube.

Beneath it a rather more adherent layer was found. This was greenish in colour, and contained both copper and zinc in

Distance in Inches from Inlet End.
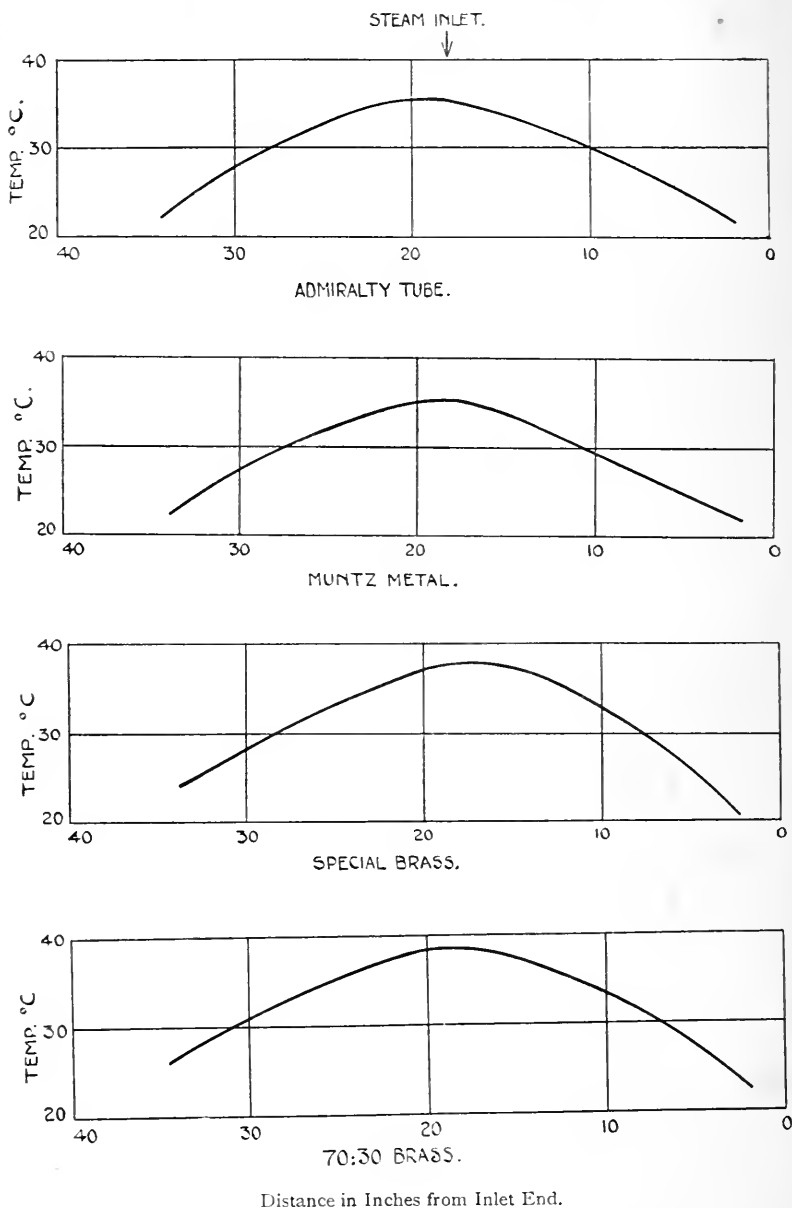
FIG. 18.—Temperature Distribution along Tubes in November.

the form of basic chloride and carbonate. In places small white spots or particles of zinc oxychloride replaced the green layer, and the tube underlying these areas was found to be dezincified. In the case of the Muntz metal tube, the green layer was normally absent and was replaced by a very thin grey-white layer of zinc oxychloride. Beneath the layer of basic salts, a layer of brown or black oxide, strongly adherent to the tube, was found in all cases.

In no case were any particles of graphite found amongst the scale. Evidently such particles as result from the dissolution of the cast-iron water-ends are washed away in the stream of sea water.

Results of the Examination of the Tubes.

ADMIRALTY TUBES, 70 : 29 : 1.

Top tube.—Dezincification in irregularly-shaped spots and areas, mainly along the bottom and sides of the tube, but extending for about 8 inches on each side of the centre.

Middle tube.—Dezincification mainly along one side of the tube. Extends for about 6 inches from centre.

Bottom tube.—No signs of dezincification.

SPECIAL BRASS, 70 : 28 : 2.

Top tube.—Dezincification at sides only. Not very pronounced. Mostly near centre of tube.

Middle tube.—A few scattered dezincified spots only. Distribution around tube irregular. Mostly near middle.

Bottom tube.—No signs of dezincification.

BRASS, 70 : 30.

Top tube.—Dezincification in spots along bottom and sides of tube, extending a considerable distance from the centre.

Middle tube.—In spots, mainly along bottom of tube. Interior surface of tube uneven, and dezincification appears to take place on the raised portions.

Bottom tube.—A large dezincified area at top of tube, near
centre.   Dezincification extends a few inches from
centre of tube.

<div align="center">MUNTZ METAL, 69 : 31.</div>

Top tube.—Severe dezincification in spots.   In some places
dezincification has almost penetrated through the tube.
Especially noticeable along sides of tube.   Most severe
near centre.

Middle tube.—Numerous dezincified spots.   One large area,
2 inches from centre.   Dezincification has penetrated
one-third through the tube in one or two places.

Bottom tube.—A few small spots at top of tube.

Note.—The formation of a pit appears to take place in the
following way.   The zinc is removed from certain spots in the
tube and leaves behind the copper in a loose, spongy, and
rotten form.   When dezincification has penetrated right
through the tube, and the copper has lost its backing of
unaltered brass, it is quickly worn away mechanically.
Mechanical, and to a certain extent chemical, action also
removes some of the copper even before dezincification has
penetrated right through the tube.   This is shown by the
measurements of the depths to which the coppery area is
depressed below the general level of the surface.

The most important deductions which the authors consider
may be drawn from this series of observations are :—

1. *The Order in which the Tubes resist Dezincification.*—The
most resistant were the $70 : 29 : 1$ and the $70 : 28 : 2$ tubes.
These appear to resist the action to about the same extent,
and were considerably more resistant than the $70 : 30$ brass,
which came next in order of merit.   The Muntz metal tubes
were decidedly the most quickly and severely attacked.

2. *The Importance of Temperature in Corrosion Phenomena.*—
In all cases the attack appeared to be most severe at or near
the centres of the tubes.   Since the steam entered the con-
densers at the centre and no baffle-plates were used, the
tubes must have been subjected to the highest temperatures
at their centres.   It becomes evident, therefore, that tem-

perature plays a most important part in determining the distribution of the areas of dezincification.

3. *Corrosion is not confined to the Bottom of the Tubes.*—It usually occurs in that position, but is by no means confined to it. It frequently occurs along the sides, and occasionally along the tops of the tubes.

4. *Graphite Particles cannot be regarded as a Cause of Dezincification.*—Dezincification can occur independently of the presence of these or any other foreign particles.

COMPARISON OF THE RESULTS OBTAINED IN THE LABORATORY WORK AND IN THE EXPERIMENTAL CONDENSER PLANT.

The agreement between the two methods of work is striking. In both the order in which the tubes resist dezincification at elevated temperatures has been found to be precisely the same.

It is unfortunate that no strictly quantitative expression can be obtained to represent the relative merit of the tubes as regards resistance to dezincification. In the case of the experiment with the condenser plant, the authors have been obliged to rely upon mere inspection of the tubes. Nevertheless, there can be no doubt that the 70 : 29 : 1 and 70 : 28 : 2 tubes are more resistant than the 70 : 30 brass, and this than the Muntz metal. The plainest evidence is afforded by the fact that one tube of each of the first two alloys completely resisted dezincification, and this indicates their superiority independently of the exact determination of the areas over which dezincification occurs, though, as a matter of fact, the total dezincified areas in these two tubes were considerably smaller than in the case of the others.

That the Muntz metal had suffered most severely was amply shown by the fact that dezincification had penetrated more than three-quarters of the way through the topmost tube in several places, and one-third of the way through the middle tube, whereas in all other types of tube dezincification had penetrated much less deeply.

The supreme importance of temperature, which had been clearly indicated by the laboratory work, was amply confirmed

by the large scale test. In each of the four sets of three tubes, the topmost was the most severely attacked, and a study of the details of the construction of the condenser will show clearly that the top tube must have been the most highly heated of each set. On the other hand, the bottom tubes of each set must have been subjected to a distinctly lower temperature than the others, and as a result the bottom tubes in two cases have not been attacked at all, and in the other two cases the attack is less than that in the case of the higher tubes.

Both sets of tests bring out the fact that the locality in which dezincification occurs is not determined by the electro-chemical action of carbon or any other foreign particles settling on the tubes. It is due to a chemical action which becomes the more pronounced as the temperature is raised from the ordinary temperature to $50°$ C., and probably higher, though the Admiralty tube must possibly be excepted from this statement. This action takes place under conditions which exclude the possibility of the settling on the tubes of any substance not derived directly from the tubes themselves.

Dezincification appears to be a phenomenon inherent in alloys of the brass type, and to be more pronounced the higher the percentage of zinc in the alloy. It starts at certain points on the tubes and spreads outwards from them, till, in time, the whole tube would become dezincified.

A distinct relation has been found between the presence of firmly adherent oxychloride and the spots or areas of dezincification. It has been observed in tubes corroded under conditions of practical work, as well as in the experimental condenser test. Direct evidence has been obtained in the laboratory as to the evil effect of this substance. The authors believe it to be both a result and an accelerating cause of dezincification.

SECTION III.

THE PROTECTION OF CONDENSER TUBES.

This subject has been but incompletely studied owing to lack of time, yet one or two interesting observations have been made which seem to be worthy of record here, since to some extent they may serve as a basis for future work.

The methods in use for the protection of condenser tubes are electro-chemical in nature; they depend either on the use of some metal, such as zinc, iron, or aluminium or its alloys, which is electro-positive to brass, and which will consequently set up an electrical current when both are connected together and immersed in sea water; or on the use of a dynamo to pass the current to the brass.

In principle the two methods are identical, viz. that of making brass which it is desired to protect, a cathode at which there will be a tendency for the liberation of hydrogen, while oxygen will tend to be set free at the anode. This anode may consist of any of the metals mentioned above. The idea is to concentrate corrosion on the anode, which is sacrificed to protect the cathode.

The metal zinc has been largely employed for anodes, both for the protection of boilers and condensers. In the case of the latter, it is placed in the water-ends and is securely bolted to the tube plates. At first sight it would appear to be a more suitable metal than iron, since it is more electro-positive, but in practice this does not prove to be the case. There appear to be two reasons for this. The first is that the zinc gradually becomes covered with a fairly adherent layer of oxide, which itself is electro-negative to brass, and is a poor conductor of electricity. Thus the protective action of the zinc soon ceases, and might even be reversed but for the poor conducting properties of the oxide. The second reason is that the consumption of zinc is found to be very great, far greater than that demanded by the requirements of electro-chemical protection. It seems probable that the zinc is subject to auto-corrosion due to the action of the zinc-oxy-chloride which adheres to the metal.

For the protection of condensers zinc has been largely replaced by iron, which is not only cheaper but more efficacious. The iron is used generally in the form of slabs, which are placed in the water-ends of the condenser, and are attached by bolts to the tube plates.

If any electro-chemical action is to occur, it is obviously necessary to ensure that the connection between the iron slabs and the tube plate be thoroughly satisfactory. It is, of course, possible that the mere presence of iron slabs in the water-ends of a condenser might give rise to a certain amount of protection by depriving the water of a large proportion of its oxygen, which will go to form rust. If this be so, no special care need be taken to ensure satisfactory electrical connections. To test this point, the following experiments were made :—

Three pieces of 70 : 30 brass tube were taken, together with three pieces of wrought iron. On to one tube and one piece of iron lengths of copper wire were soldered. These were weighed separately, and then the copper wires were connected together, so as to ensure good electrical contact, yet they could be separated again for weighing purposes. The tube and iron were then immersed in a beaker containing $1\frac{1}{2}$ litre of sea water.

One of the other pieces of brass tube was weighed, and suspended in another beaker at a depth of 2 inches from the surface. At a distance of $\frac{1}{2}$ inch above it a weighed piece of wrought iron was arranged. Thus there was no electrical connection between the tube and the iron.

The other length of tube and iron strip were similarly immersed in a third beaker through which a stream of air was kept bubbling. The air was introduced at the bottom of the beaker.

All the beakers were then placed in a thermostat at $50°$ C. The object of carrying out the experiments at this temperature instead of at the laboratory temperature, was to ascertain whether electro-chemical protection would prevent selective corrosion, which is particularly active at this temperature. At the end of 7 and 14 days all the pieces of metal were weighed, and the results are given in Table X.

It will be seen that the tube which was in electrical contact

with the iron was completely protected, since it shows no loss of weight. The surface appeared quite bright and unoxidized and no sign of pitting could be seen, although experiments described elsewhere in this paper show that it occurs normally in seven days at this temperature. On close examination, the protected brass tube was found to be covered with a uniform thin transparent layer of some substance, which could only be removed by scraping. The layer was of about the thickness of tissue paper, and proved to consist of calcium carbonate. The rôle of this layer evidently deserves careful consideration in any discussion on the mechanism of protection.

TABLE X.—*Protection Experiments in Sea Water at* 50° *C.*

	Interval.	Immersed in 1½ Litre Sea Water and Electrically Connected.		Not Connected. Non-aerated.		Not Connected. Aerated.	
		Brass and Wire.	Iron and Wire.	Brass.	Iron.	Brass.	Iron.
Initial weight in grammes . . Weight after . .	... 7 days	24·1859 24·1859	12·8052 12·5200	21·1220 21·1035	11·6890 11·5816	22·3108 22·2740	10·0216 9·8750
Loss in grammes	...	...	0·2852	0·0185	0·1074	0·0368	0·1466
Weight after . .	14 days	24·1859	12·3040	21·0910	11·4640	22·2360	9·6570
Total loss in grammes . .	...	...	0·5012	0·0310	0·2250	0·0748	0·3646

Neither of the other tubes was completely protected by the iron. The general result of the experiments therefore confirms the view which is generally held, that good electrical connection between the iron and brass is necessary for the protection of the latter. The tube suspended in the aerated beaker showed severe dezincification on the back and sides, while the other tube was slightly attacked at the edges and on a few scattered spots on the back. The attack was somewhat less severe than would have been expected if there had been no iron in the beaker, but the protection afforded by the latter was slight.

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In the experiments just described the iron was arranged close to the brass, so that the conditions were especially favourable for protection.   In a condenser containing tubes 16 feet long, on the other hand, the iron slabs—even when used in both water-ends—must exert a protecting influence over a distance of 8 feet of tube, if the protection is to be effective in the middle of the tube.   It seems, at first sight, a little difficult to understand how the protective action of the iron can extend thus far, since, on the electro-chemical view, the protection afforded is proportional to the current passed, and the current passing round the iron-seawater-brass circuit must be very small, owing to the considerable internal resistance of the circuit.   Moreover, it seems as if the greater part of the current would pass through the water to the *tube plates*, and so back to the iron through the condenser body ; only a minute current would pass through the water to the tubes, and so back to the iron *via* the tube plate and body.

The exact amount of current conveyed to any portion of the tube can be readily calculated from the resistance of the seawater circuit through which the current must pass to reach it.   The resistance of this circuit increases rapidly as the distance up the tube increases, and at a distance of 8 feet up the tube the amount of current passing to the last few inches of tube must be extremely small.   Consequently, it is difficult to see how iron slabs in the water-ends can protect the middle of the condenser.

The same difficulty is met in considering the mode of protection by a current generated by a dynamo, as in the Cumberland process.   Of course, in this case a much larger current can be used, and it can be increased at will until it is effective, but the authors have been informed by Mr. Cumberland that in normal cases two ampères per 1000 square feet of tube surface is sufficient for protection, and where such a small average current is used the amount conveyed by the most remote foot of tube will be very small.   It seems certain that some other factor must operate to assist protection.

To test the matter the following experiment was made :— A glass vessel of the shape shown in Fig. 19 was obtained and filled with sea water.   In it were placed three lengths of

70 : 30 tube B, C, D, soldered to leads of copper wire, and three of these were connected to a single iron anode, A, and a delicate milliammeter was included in the circuit. The arrangement merely amounts to placing three brass cathodes at three different distances from the anode. These distances were $\frac{1}{2}$ inch, 10 inches, and 20 inches respectively. A fourth piece of tube, E, was placed in the apparatus at the point farthest
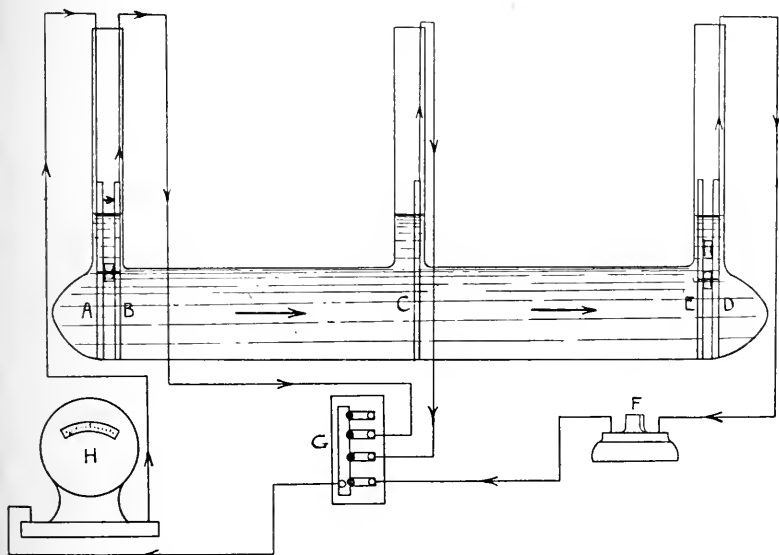
Fig. 19.—Apparatus for Protection Current Experiment.

from the iron, but was insulated from the other piece D, and from the iron, and served as a check.

It will be noticed that the distance of the farthest tube from the iron anode was forty times as great as that of the nearest. Its area was twice as great, hence the average amount of current conveyed by the farthest cathode was approximately one-twentieth of the current conveyed by the nearest. In an ordinary condenser, if the protector blocks be situated 4 inches from the tube plate and the centres of the tubes be 8 feet away from the tube plate, the last 3 inches of the tube will convey—on an average—one twenty-fourth of the

total current, or approximately the same proportion as in the experiment now being described.

At the beginning of the experiment the milliammeter was introduced into the main circuit, thus the total current passing to and from the iron anode could be measured. When the circuit was first closed the indicator needle gave a slight kick and returned to zero and remained there. If the circuit were broken and remade after a minute or two, the needle again showed a slight kick and returned to zero, and the result could be repeated as often as desired. Evidently polarization prevented any current flowing continually round the circuit.

At the end of three weeks the brass tubes were examined. It was found that each of the three tubes connected with the iron was covered with a thin translucent layer of calcium car-bonate. This layer showed a very slight pinkish tinge, due, apparently, to the mechanical entanglement of particles of ferric oxide which were present in the sea water in the apparatus. Underneath the layer the brass was found to be bright and unattacked in all three cases.

The piece of brass used as a blank was covered with a layer of brown oxide such as is ordinarily met with in experi-ments carried out at the ordinary temperature. No layer of calcium carbonate had been deposited upon its surface. Evi-dently the passage of a current is necessary for its formation.

It seems to be formed in the following way :—Immediately the circuit is closed hydrogen ions will pass out of solution at the cathode. These ions have been in equilibrium with bicarbonate ions in the solution ; consequently the bicarbon-ate ions will break up and yield hydrogen and carbonate ions till equilibrium is restored. Owing to the low solubility product of $CaCO_3$, this release of CO_3 ions will cause the precipitation of $CaCO_3$ on the cathode in the neighbour-hood of which the reactions are taking place. The layer of calcium carbonate thus formed will interpose a large resistance into the circuit, and the current will be reduced practically to zero.

The manner in which iron anodes can afford protection to the tubes over great distances from the anodes themselves, now becomes evident. The greater part of the protecting

current passes at first by the shortest path and protects only the parts near the iron anodes. These soon become covered with a layer of calcium carbonate, which greatly increases the resistance of that path; consequently the current passes to more remote but bare portions of the tube and covers them with the same film. The process is repeated, and the protecting layer of calcium carbonate creeps gradually along the tube. The extreme distance over which protection can be afforded in this manner is conditioned by the relative resistances of the layer of calcium carbonate and the increased resistance of the path of water through which the current must pass to reach the more remote parts of the tube. When the latter becomes greater than the former the protection will cease.

The part played by the film of calcium carbonate in electro-chemical protection must be very important. It is effective in preventing both the complete and the selective types of corrosion. It even prevents, to a great extent, the initial step towards corrosion, viz. oxidation of the metal. The film appears to be hard, uniform, and adherent and by no means easily broken mechanically. It should be remarked, however, that the experiment in which it was formed was carried out in stagnant sea water, *i.e.* under conditions in which mechanical injury was not likely to occur. It deserves to be repeated in running sea water.

The question may fairly be asked, how can corrosion ever occur when iron slabs or an external current are used for protection? The answer is that it can occur apparently in several ways:—

1. By the breakdown in the electrical connections between the slabs and the tube plates, and this may occur by the oxidation of the bolts, nuts, &c.

2. By mechanical injury to the layer of calcium carbonate caused by iron cleaning rods, passage of sharp particles through the tube, &c.

3. By the failure of the calcium carbonate to adhere firmly to the tube, especially if the latter has first undergone slight oxidation and corrosion.

The precise conditions under which this film can be formed and maintained deserve further study.

General Summary of Experimental Work.

All the conclusions tabulated below are based on experiments carried out with natural sea water and ordinary condenser tubes of commerce.

1. The alloys examined corroded in two distinctly different ways, one of which is characteristic of ordinary atmospheric temperatures—termed " complete corrosion," and the other of temperatures slightly elevated—termed " selective corrosion."

2. Selective corrosion, which results in dezincification and pitting, and is therefore the cause of the practical problem, *must be regarded as an inherent property of the alloys examined, provided that sea water and the requisite temperature conditions are present.*

3. The influences of a number of the deposits and particles hitherto supposed to be the causes of dezincification have been shown to be unimportant.

4. The influence of the juxtaposition of two phases in the alloys examined was found to be unimportant.

5. The order in which the alloys resisted complete corrosion was different from that in which they resisted selective corrosion. Hence the resistance to selective corrosion cannot be deduced from observations on the resistance to complete corrosion at the ordinary temperature.

6. The results of the experiments with the model condenser plant confirmed the results obtained in the laboratory experiments.

7. Preliminary observations have been made upon the mode of action of electro-chemical protection, and attention has been directed to the deposition of calcium carbonate scale on protected tubes.

Some Observations on the Practical Problem.

It has become clear from the experimental work previously described that dezincification followed by pitting is a phenomenon inherent in brass alloys of the type discussed.

The conditions for its appearance are the presence of certain kinds of water, of which natural sea water is one, and of a certain temperature.   The physical state of the surface of the alloy may have some influence in determining the exact points at which the action starts, but merely assists a tendency which is characteristic of the alloy.   The action once started will spread throughout the alloy.

Dezincification may be prevented, or at least postponed, by four different means:—

1. By using a suitable water supply.
2. By using an alloy different from brass.
3. By adjustment of the temperature conditions when brass is used.
4. By electro-chemical protection.

In the mercantile marine Method 1 can never be employed, and it can rarely be used even in land installations.   Moreover, there is, as yet, no precise information as to the kinds of water which will not give rise to dezincification.

As regards Method 2, very little information is at present available.   An obvious suggestion is to lower the amount of zinc present in the alloy, and thus to diminish the tendency towards dezincification.   As to how far, if at all, the elimination of zinc could be usefully carried, the authors cannot make any definite statement.   It is, however, certain that a complete removal of zinc would give rise to serious trouble of another kind.   Possibly there may be some alloy intermediate between 70 : 30 brass and pure copper which would be more resistant to corrosion than either, though whether it could be satisfactorily drawn into tubes is another matter.   Probably manufacturers have already experimented privately along these lines, and information on the subject would be welcomed.

A number of alloys which contain no zinc suggest themselves as suitable for the manufacture of condenser tubes. Phosphor-bronze has been proposed on a number of occasions. It can be drawn into tubes of good quality, and at first sight would appear to be an excellent material for the purpose. Under certain conditions, however, it appears to be subject to a peculiar and deeply penetrating form of complete corrosion, the cause of which has not yet been ascertained by the

authors, and the phenomenon of " detinning " has also been observed. More work upon this alloy is desirable before it can be recommended for use.

A copper-nickel alloy produced on a large scale in America, and known as "monel metal," has been used for condenser tubes. It appears to give satisfactory results as far as resistance to corrosion is concerned, but its high price has prevented its extended use.

The work of Carpenter and Edwards * would suggest the use of a copper-aluminium alloy if it could be easily and cheaply drawn into tubes, but the authors have never had an opportunity of experimenting with tubes of such material.

As regards the immediate future, and pending future investigations on different types of alloy, the best means at the disposal of engineers for hindering corrosion appear to be :—

1. The entire abandonment of the use of plain 70 : 30 brass, and its replacement by either the Admiralty alloy, 70 : 29 : 1 (tin), or Muntz's special brass, 70 : 28 : 2 (lead).

2. Careful control of the temperature in condensers.

3. The extended use of electro-chemical protection.

As regards 1, ample evidence will be found in the experimental section of this report, and the matter needs no further emphasis here.

As regards 2, the authors consider that the importance of temperature in determining the nature of the corrosive attack on brass by sea water has not received from engineers the attention it deserves.

In practice the most important factor which influences the temperature in a condenser is the amount of steam admitted to it. This may be conveniently stated as the number of pounds of steam condensed per hour per square foot of tube area. Inquiries have been made by the authors as to the average amount condensed in ordinary practice, but they find that engineers are rarely able to state the amount, though they can usually state the amount of steam the condenser was originally constructed to deal with—a somewhat different matter.

* *Proceedings of the Institution of Mechanical Engineers*, 1907, p. 57.

In the authors' work with the experimental condenser the temperature of the outlet water rose to 40° C. in hot weather, when only 5 lb. of steam were being condensed per square foot of tube surface. The temperature of the hottest part of the tube rose under the same circumstances to 55° C. Even in cold weather the temperature of the hottest part of the tube approached 40° C., which is in the danger zone. The temperature of the outlet water was then almost 25° C.

The table given on pp. 16 and 17 shows that the temperature of the outlet water of ships trading to the tropics averaged about 42° C., and of other ships about 36° C. It is probable, therefore, that the temperature conditions in the experimental plant were somewhat less severe than in the condensers of ships in the Atlantic and cross-Channel trades. It is particularly noticeable that in case No. 12 of the table, 100 per cent. of the tubes failed in four years, and the temperature of the outlet water was in this case the highest recorded.

In the tables the temperatures of the outlet water vary from 68° F. to 130° F. Part of this variation is, of course, due to variations in the temperature of the intake water, but part is due to conditions which can be controlled.

The temperature of the water in a condenser can be kept down in the following ways :—

1. By limiting the amount of steam condensed.
2. By shortening the path of the water through the condenser.
3. By increasing the speed of the water.
4. By preventing choking of the tubes, either by fitting screens or filters, or by frequent cleaning.

As regards 1, the amount of steam condensed has been considered hitherto from the point of view of engine-efficiency and space-economy, and not at all from the corrosion standpoint. Nevertheless, it is a fact that, within the practical limits of temperature,* the greater the amount of steam condensed the greater will be the tendency to selective corrosion, and if the condenser be really overloaded this form of corrosion may be extremely rapid.

* It is probable that at high temperatures the speed of selective corrosion falls off again, and finally becomes zero, but these temperatures are almost certainly too high for effective steam condensation to take place.

The effect of temperature has been completely masked in recent years because of the peculiar distribution of temperatures in condensers arising from the use of baffle-plates. When these are used the hottest part of a tube is not necessarily the middle of its length, but may be almost any part between the middle and the last foot or two. Its position will be determined by the size of the baffle-plates and the velocity of the steam entering the condenser.

The explanation of the extremely long life of the tubes in a Yarmouth trawler, to which reference has already been made, is probably due to the fact that the vessel was normally under easy steaming conditions, and consequently the amount of steam condensed per square foot of tube surface was very small, and the temperature in the condenser low.

As regards 2, the practice of dividing a condenser into two " nests " is a distinct aid to corrosion. As the water passes through the lower nest it becomes heated, and consequently the top nest is supplied with water that is already warm and which will become still more highly heated. From the corrosion point of view it would be preferable to introduce a separate water inlet and outlet to each nest of the condenser, and to discontinue the practice of building them in nests (especially since the condensing efficiency of the tubes in the lower nest is small).

As regards 3, inquiries have shown that the speeds of water through the condensers in the mercantile marine vary between 240 and 360 feet per minute. The average for all the figures obtained is about 290 feet per minute. The speed of the water used in the experimental plant was about 275 feet per minute. The faster the speed of the water in the condenser the lower the temperature, other things being equal, and the less the liability to the choking of tubes. In the authors' opinion the speed should be kept up at least to the highest figure mentioned above, and it might be worth while to try still higher speeds.

Inquiries made by the authors have shown that choked tubes are sometimes severely corroded, and sometimes not at all. If a choked tube be found in the bottom part of the condenser working normally it will not usually be corroded,

since its temperature, even in this case, is still low; if, however, the condenser is being overloaded, as shown by the high temperature of the outlet water, it may be severely corroded. If a choked tube be found in the top part, however, it will usually show severe dezincification, owing to the high temperature to which it has been heated. Hitherto the corrosion of choked tubes has been attributed to the electro-chemical action of particles, more particularly of carbon, but this view has now been clearly shown to be untenable.

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DISCUSSION.

The PRESIDENT, Professor A. K. Huntington, Assoc.R.S.M., in calling upon Dr. Bengough to present the Second Report to the Corrosion Committee of the Institute of Metals, said he would like to say what an admirable report he considered it was, and they would all agree with him that it was drawn up on exactly the right lines for such a Report. It did not claim more than was warranted by the evidence, and it set forth its facts in a business-like, straightforward manner.

Dr. BENGOUGH, in introducing the Report, said that he feared they would consider this a lengthy document, but it contained the result of about two years' work by himself, and in addition, since last October, Mr. Jones had spent his whole time on it. It was a record of a very large amount of work, and it was difficult to condense a Report of that kind, because if one did, one very often missed out those very points which people interested in the subject wished to know about. He thought that was one of the reasons why, in the past, there had been so much conflict of opinion as to the causes of corrosion. The papers did not contain sufficient accounts of experimental details to enable any one to judge exactly the value of the experiments recorded, and that had helped to make the investigation of the subject of corrosion very confusing, and at times conflicting data were given. So they had decided to give full experimental data. It appeared to him that in one or two parts of the Report there was even now not sufficient experimental data given, so he had brought a considerable stock of additional facts and figures which could be shown to anybody who required them.

A word was due to Mr. Jones, his collaborator. Mr. Jones was a research student in his (Dr. Bengough's) laboratory until quite recently, but he regretted that the Corrosion Committee had now been deprived of his services, owing to his having received a Glasgow appointment under Professor Campion. They might be interested to know that Mr. Jones obtained his degree of M.Sc. for some of the work done in connection with this Report.

He found on examination that there were a number of minor verbal slips in the text of the Report, but they would be corrected before the paper appeared in its final form ; they were quite small and unimportant, and he thought that in no case did they confuse the meaning.

There was a statement on p. 28 which appeared to require a little additional explanation. The Report stated :

" The copper and zinc are attacked in approximately the proportion in which they occur in the alloy."

That was a somewhat important statement. In an earlier part of the Report they had stated that they started research work with a view to finding out the amount of dezincification, if any, that took place when brass was attacked by sea water. Their conclusion was put in a rather qualitative way, and he would like to mention the experimental basis they had obtained for that conclusion. The copper and zinc in the

deposit formed on brass tubes were estimated, and the proportions were given on p. 29 at the foot of the page. They found in the deposit 40 per cent. of copper, 13 per cent. of zinc, and a certain amount of chlorine and carbon dioxide which, as they would see, totalled altogether only to 60·59 per cent. The oxygen in combination with the zinc and the copper would increase the percentage and would bring it up to about 70 per cent. ; the balance would be mainly magnesium and calcium, as mentioned in the paper. They had next attempted to estimate the zinc that had passed into solution in the sea water. The estimation of zinc in sea water was not an easy matter, and they adopted a rather novel process which he would like to describe. To the sea-water solution they added sodium carbonate to precipitate the heavy metals. Then they dissolved the carbonates in sulphuric acid, and added a solution of potassium sulphate and potassium oxalate. The precipitate of calcium oxalate was allowed to settle before proceeding. Then they got the zinc out of the solution by the electrolytic process, the solution being electrolyzed straight away. They had obtained very fair deposits of zinc by that method. But it was not absolutely accurate, because in some cases the zinc came down rather dark in colour. That was why they had not printed exact details. Though the method was not absolutely satisfactory, yet the results were sufficiently accurate, and they agreed with one another well enough to show that if there were any preferential solution of zinc it was very little. The amount of zinc they got from the solution turned out to be very nearly equal to the amount in the deposit. At any rate, they felt quite sure that if there was any preferential solution of zinc, it was very slight indeed.

The next point he would like to speak upon related to p. 41, where they remarked with regard to the figures illustrated there :

" It is very noteworthy that the 70 : 28 : 2 brass did not show any sign of this selective attack under these conditions, while, of the others, Muntz metal seemed to be the most susceptible to it."

That afforded strong additional proof of the uselessness of the ordinary loss-of-weight method in estimating the merits of tubes from the anti-corrosion point of view. Although the experiments were carried out with diluted sea water only at the ordinary temperature, they were clearly quite sufficient to show that the loss-of-weight method was no good at all as regards selective corrosion. Muntz metal suffered most from dezincification, but as regards general corrosion Muntz metal was the best alloy they examined. In the other experiments described in the paper there was little to choose between the Admiralty metal and the lead-tin alloy, but in that particular test the lead-tin alloy came out superior to the Admiralty metal. They were still continuing their experiments, but as far as they had gone at present the lead-tin alloy was the best as regards all-round resistance to dezincification.

The CHAIRMAN pointed out that the Report did not mention that it was a lead-tin alloy, and he thought it ought to be emphasized, that one of the alloy metals was lead.

Dr. BENGOUGH pointed out that the analysis of the metals was given on p. 67. That table showed the complete analysis of the alloy to which he was referring, which was the second in the list.

On p. 45 there were some particulars given about the rate of corrosion when flowing sea water was used, and the curves were given on pp. 46 and 47. The curves began by being practically straight lines in both cases ; but after twenty-one days the curves began to bend over, and that change appeared to be due to the fact that after three weeks the green deposit began to stick tightly to the tube, and if they tried to remove the deposit they ripped off some of the underlying oxide.

On p. 49 they referred to some experiments that had been carried out with the jelly indicator, such as was used by Walker and others with iron and steel. But they could not get any satisfactory results from those experiments. The ferrocyanide contained both copper and zinc. Both the copper and the zinc passed into solution, and they got a brown layer of metallic ferrocyanides. It was brown, in fact, because it contained copper which marked the appearance of the white zinc ferrocyanide.

On p. 50 they dealt with the conclusions to be derived from the experiments carried out at an ordinary temperature, and they stated :—

"Particles such as carbon in the form of coke, coal, or graphite, sand, &c., have little or no effect on the speed, or type, of corrosion."

There was a slight effect, because they afforded a kind of mechanical protection to the tubes, and so the loss was probably less than if those substances were not there.

There were one or two small matters which might be added to those conclusions, and one in particular which he intended to add as number 9. It was particularly interesting, and he did not know how he had managed to omit it from the paper. That was the effect of work on the tubes. That subject had been frequently dealt with, and it was often thought that a hard tube would lose more in weight than one rather softer. Sir Gerard Muntz was good enough to supply them with two tubes, one drawn down more than the other, but both in process of being drawn down. Both were subjected to experiments, in comparison with a finished tube, to see whether the additional drawing which was put on the finished tube would have any effect on the corrosion. They found there was practically no difference in the rate of corrosion between the three tubes. The partly-drawn tubes lost practically as much in weight as the finished tubes, and evidently work had not a very important effect.

Another experiment, which was also due to a suggestion of Sir Gerard Muntz, was carried out on tubes covered with a thin film of metallic copper. They had been placed in a pickling bath. The pickle had become very concentrated as regards copper, and some of it had plated out on to the tubes. They thought that it might affect the rate of corrosion. It was only another form of the copper plug experiment, described in the paper. In both cases they got quite negative results.

While the copper tubes corroded rather slower than ordinary tubes, the effect was very, very slight indeed.

On p. 57 they said in the second paragraph at the end :—

"On the other hand dezincification began at certain definite spots and spread gradually. At these spots white basic chloride of zinc was formed, and adhered firmly to the tubes. The nature of the action seems to the authors to be as follows."

Well, the following paragraph expressed their idea as to how that action could take place locally, but there was no doubt about it that that was not altogether a sufficient explanation to account for the points at which corrosion began. They did not think it fully represented the matter, although it probably had some bearing on the point. He was inclined to think that the real effect in practice was that there existed in alloys certain reactive areas, which were more susceptible to chemical activity than the neighbouring areas. Chemical reactions would begin at those areas, and spread gradually outwards. Chemical reactions in general began by changes in certain molecules which reacted more readily than others. They did not take place explosively by all the molecules reacting at once. They began at certain definite points, and certain definite molecules reacted before others. He believed that brass tubes showed that action, and that some areas reacted more readily than others, but why they did so was beyond their present means of investigation; they could not at present distinguish between the several molecules of the same substance as regards chemical reactivity. It was, therefore, impossible to predict the exact spots at which corrosion would begin, but when it began it would go on at that area as explained in the Report. They could not explain adequately the differences between neighbouring areas, and he did not expect that tube makers would be able entirely to get over the difficulty of localized corrosion until they knew a great deal more than they knew at present about the nature of chemical reaction.

With regard to the protective influences of tin, lead, &c., they had not been able to form any very satisfactory theory, for the undoubted fact that tin and lead do retard corrosion of the selective type. In a paper to be read at that meeting, Dr. Desch suggested that tin formed a sort of protective paint over the metal, and so prevented corrosion, but he had dealt solely with alloys consisting of the β-phase. That phase had scarcely been dealt with in the Report, but Muntz's metal contained a certain amount of the β-phase. As regards their own experiments, they did not think that the idea of the coating of tin was altogether a satisfactory explanation, because that coating did not prevent total corrosion, but only prevented dezincification. Personally, he thought tin must have some other action than that of a protective paint. The question of how it operated must be left for future work.

In regard to the statement on p. 69 as to the closing down of the condenser plant, he would like them to understand the condition in which the plant was left. The plant had been taken to pieces, the

end of the condenser taken off, the tubes removed, and the whole apparatus very carefully dried, so that any corrosive action must have stopped, and the apparatus was removed and stored in a place where no damp could possibly come. The effect of that was that if they were to continue the experiments they might regard the gap of time between the time of stoppage and starting as merely lost time. If anybody had any criticism to offer in regard to that, he would be very glad to hear it, but they adopted what they believed to be the best course, and left no water to carry on reaction. As far as they could see, the only possible source of error was the hygroscopic action of the deposit in the tubes. Those were the chief points to which he would like to draw attention. If gentlemen interested would inquire as to details, other than those given in the paper, they could be supplied.

The PRESIDENT, in calling upon Sir Gerard Muntz to open the discussion, said that, as Sir Gerard was Chairman of the Corrosion Committee, he was sure they would be very willing to extend the time limit to some extent.

Sir GERARD MUNTZ, Bart. (Past-President), said that the result of Dr. Bengough's report was that they had to revise the whole of their preconceived theories on the subject of the action of corrosion of brass condenser tubes by sea water.

The cause which had in the past been most usually ascribed as the reason of the pitting of condenser tubes, namely, the presence of deposits in the tubes containing iron and other foreign ingredients, had been shown by Dr. Bengough to be of little consequence—in fact negligible. Galvanic action was considered generally to be the usual cause of pitting. The question of dezincification was little understood, and had hitherto been very slightly studied by those interested in the life and wear of condenser tubes.

Accurate information as to the conditions of service of tubes, and the relative localities of the points where corrosion took place, had been hard to obtain. Engineers had either been disinclined to take the trouble to ascertain or define these points, or had not had sufficient knowledge on the subject to enable them to deal with the matter in an intelligent and intelligible manner.

Thinning of tubes was totally distinct from pitting. Thinning might arise from two causes—the mechanical cutting action of water, which usually showed most at the intake ends of the tubes, or from electrolytic action set up by short-circuited electric currents, which caused a total dissolution of the brass—in such cases certain tubes which received the full charge of the short-circuited current were thinned from end to end, until, if left long enough, they were completely worn through by the total dissolution of the metal.

The table of information from inquiry schedules was very interesting, but to be of real value a complete analysis of each failed tube was necessary.

The suggestions by firms as to causes of corrosion were decidedly curious, especially No. 1, where the cause suggested was, "Tubes not now made of the same clean alloy as formerly." This was diametrically opposed to facts, for as a matter of fact the copper and zinc *now* used in the manufacture of tubes was far purer and cleaner than was formerly the case, for the simple reason that fifteen years ago it was difficult to obtain either copper or zinc which did not contain a very considerable admixture of impurities. The nature of failure in case No. 1 was stated to be dezincification, which pointed (in the light of Dr. Bengough's report) to the reason of failure having been that the tubes were made of *too pure* ingredients. This example only showed how dangerous it was to jump at conclusions, without sufficient knowledge of the subject.

With regard to carbon particles, a long experience and much careful investigation and examination by analysis and under the microscope had taught them that the inclusion of carbon particles in brass tube castings was very rare; in fact, such cases were conspicuous by their absence. The specific gravity of carbon was very low as compared to that of brass, and it was therefore obvious that any carbon particles which might be worked into the brass from the cores or the dressing of the moulds would float to the top and be cut away with the gate. As a matter of precaution against the probability of carbon particles being retained by the brass, the speaker, some years since, had the use of carbon-dressed cores discontinued at the works which he controlled (Muntz's Metal Co.'s), and, as far as possible, eliminated the carbon from the dressing of the moulds.

The uneven distribution of temperature throughout any condenser would be sufficient to account for the preferential attack by dezincification of certain tubes.

The failure of condenser tubes by total dissolution or thinning was rare; in 90 per cent. of the cases of failure the cause was pitting, that was to say, preferential dissolution. The method of experiment adopted in the laboratory by Dr. Bengough seemed to have been ingenious, simple, and a fair practical representation of the actual conditions which the brass would undergo in the usual run of practical work.

The results obtained at normal temperatures, and shown in Tables II. and III., p. 24, were interesting, and might prove of value in other directions; but, as far as the investigation of the failure of condenser tubes went, these were of little value, because such temperature would not exist in any condenser when at work; its only value was to show what action might occur if a condenser was left standing cold with the tubes full of water.

On p. 31, section 6, paragraph 2, a very interesting point was brought out, namely, that the presence of slight flaws in the metal had no effect upon the corrosion. That was to say, that it by no means followed that corrosion would preferentially start at the flaws. Another point of interest referred to on p. 31 was the action of CO_2 on brass. This was a matter

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which might have a very important bearing on the wear of condenser tubes in land installations, where other than sea water was used.

On p. 32 the Report referred to the lesser total dissolution of Muntz's metal as compared with 70 : 30 brass. This one would have expected ; it was this superiority of Muntz's metal to brass in its powers to resist sea water action in the form of total dissolution, which first brought Muntz's metal into prominence as a medium for ship sheathing. In this second series of experiments, only total dissolution was obtained, and there was apparently no preferential dissolution of zinc. Speaking as a tube-maker, he was glad that condenser tubes did not work under such conditions, for if tubes lasted seventy-five years makers would be very short of orders.

With regard to the tests in diluted sea water described on p. 40, the preferential or selective corrosion of zinc from all the samples (except 70 : 28 : 2) was important as bearing upon the question of the failure of condenser tubes using such water, as, for instance, in ships running in river estuaries, or in power plants using estuary or harbour waters.

The failures of condenser tubes in such situations were far more frequent than amongst ships running in open water, and this in itself was strong evidence in support of the accuracy of the results obtained by Dr. Bengough and referred to on p. 41.

The remark that Muntz's metal showed itself as most susceptible to this action of diluted water was of interest, and was borne out by the fact that far more trouble from corrosion had always been prevalent in Muntz's metal sheathing used in river estuaries and harbours than where used on open sea-going ships, more especially in tropical and semi-tropical waters, though some of the most aggravated cases occurred in the Thames Docks some forty or fifty years ago, but this case might have been influenced by other causes.

As to the presence of particles, it would appear that Dr. Bengough's investigations had pretty completely eliminated the question of the detrimental action of particles from the discussion, and that for the future they might strike out that element in the course of their research.

With regard to the experiments at the temperatures 40° and 50° C., the change in the order of resistance of 70 : 29 : 1 brass, 70 : 30 brass, and Muntz's metal with the increased temperature was remarkable. One point of special interest to him was the statement that at the increased temperature of 40° C. the surface of the Muntz's metal sample remained perfectly bright and untarnished. It was a fact established by long experience that where dezincification was taking place rapidly in Muntz's metal there was no green deposit of oxychloride of copper formed ; the metal remained of a yellow or pale blue buff tint. The appearance of such sheets was in itself a sufficient indication that dezincification had set in. This trouble had during the past fifteen years been very frequent, especially in tropical and semi-tropical waters. Until the year 1898 it was almost unknown. This date was of importance, because it synchronized with the introduction of the manufacture and generally

increased use of electrolytic copper. The best selected copper and the "special" zincs of former times contained a considerable admixture of lead, frequently amounting to from 1 per cent. to 2 per cent., but the introduction of electro-deposited copper and the improvements in zinc refining markedly reduced this admixture. These facts had a significant bearing on the results obtained from the 70 : 28 : 2 lead brass which had resisted selective corrosion in such a marked degree. In the case of dezincification of Muntz's ship-sheathing metal, the surface of the metal was often covered with a white incrustation of small spots from $\frac{1}{4}$ inch to a pin's point diameter ; and sheets showing this incrustation were invariably dezincified, often throughout the whole sheet, and absolutely rotten. It was in seeking to find a remedy for this trouble of dezincification of Muntz's metal sheathing that the introduction of a percentage of lead was first thought of and tried with markedly improved results. Users had, like the engineer in No. 1 of the schedule of inquiries, attributed the failure of sheathing to all manner of defects in manufacture, and most frequently to the use of cheap and impure materials. The officials of Muntz's Metal Company were conscious that not only was *more* care exercised in the manufacture in every phase, but also that the raw materials used were far purer than had ever formerly been the case. It was only after vainly seeking the cause in all sorts of directions that it occurred to them *that the metal was too pure.* Examination of certain sheets returned from Australia after forty years' use in sea water, in practically as good a condition as when first put to work, and only very slightly worn away, showed that this alloy was by no means free from foreign admixture of metals, and that the chief of these additions was lead. Laboratory experiments soon proved that by adding lead this selective dissolution of zinc could be retarded, if not entirely stopped. It was from this beginning that the 70 : 28 : 2 lead tube was evolved as an antidote to the trouble of condenser tube pitting. A very short experience showed, that although total dissolution still continued, there was no selected corrosion of zinc, *and that there was no pitting with these tubes.* Some remarkable cases of its efficacy had been experienced ; in one case, where every previous class of condenser tube had been tried and had failed in six months, Muntz's Nergandin (70 : 28 : 2) tube was put in, and had been at work ever since, now some four years, without any sign of failure.

On p. 24, Dr. Bengough referred to the accelerated action of preferential corrosion on the sawn edges of certain tubes. In the case of Muntz's metal it had been abundantly proved that thorough annealing at temperatures from 650° to 800° did prevent the preferential corrosion of zinc. Further, it was established some seventy-five years ago that cold-rolled Muntz's metal became rotten and brittle after a very short period of immersion in sea water, and that it was absolutely essential that all ship sheathing should be carefully annealed. This matter of the effect of annealing in the question of selected corrosion required close and careful scientific investigation to ascertain the cause of the difference. The sawing of the tubes, referred to on p. 54 of the Report, would

mechanically harden the edges, and this might possibly be sufficient to account for their being first attacked in that portion.

The order of resistance to dezincification, as set forth by Dr. Bengough on p. 56, tallied curiously with Muntz's Metal Co.'s experience, and was supported by the previous remarks.

A series of laboratory experiments which Muntz's carried out with the qualities of brass tubes, namely, 70 : 30, Admiralty, 70 : 29 : 1, and Muntz's Nergandin, 70 : 28 : 2, had resulted as follows :—

The specimens were placed in beakers in sea water, and a low potential electric current was applied. Carbon cathodes were employed. The tests lasted sixty-six days, and gave the following results :—

Alloy.	Original Percentage.		Resultant Percentage.	Excess Loss in Zinc, per Cent.	Loss in Grammes.
70 : 30 brass .	Copper .	70·65	71·6	0·93	0·587
	Lead .	0·33			
	Iron .	0·14			
	Zinc .	25·91			
Admiralty alloy, 70 : 29 : 1 .	Copper .	69·5	70·00	0·50	0·700
	Lead .	0·31			
	Iron .	0·17			
	Zinc .	25·97			
	Tin .	1·05			
Muntz's Nergandin, 70 : 28 : 2 lead . .	Copper .	69·7	69·19	0·09	0·689
	Lead .	1·6			
	Iron .	traces			
	Zinc .	25·7			

The order of preferential solution of zinc in this series of experiments coincided closely with the results obtained by Dr. Bengough. The greatest total loss was in Admiralty ; the least in 70 : 30. Nergandin was scarcely at all dezincified. From the result of their experiments and larger commercial experience, Muntz's were brought to the conclusion that the addition of from $1\frac{1}{4}$ per cent. to 2 per cent. of lead was the solution of the preferential corrosion puzzle. Lead up to a $\frac{1}{2}$ per cent. appeared to be harmful. Lead from $\frac{3}{4}$ per cent. to 1 per cent. appeared to be neutral. Lead from $1\frac{1}{4}$ to 2 per cent. was beneficial. The combination of lead and tin in brass was detrimental.

The deposit of green oxychloride referred to on p. 57 was washed off by the passage of sea water. This erosive action might be readily observed on the bows and bilge of a sea-going ship sheathed with Muntz's metal—the same effect would probably be obtained in a condenser tube if the water were circulated sufficiently rapidly, and the danger from the deposition of oxychloride of zinc must be thus much reduced.

The fact that at temperatures even as low as 25° C. 70 : 30 brass was attacked by selective corrosion, pointed to the undesirability of this alloy for use as condenser tubes. The temperature of a condenser always exceeded this.

Total dissolution was a matter of small account, for, as Dr. Bengough had pointed out, if only this were to be contended with, a condenser tube would last seventy-five years. It was evident that at 50° C. the action of selective corrosion was much more virulent; but it was also evident that the presence of 1 per cent. of tin or 2 per cent. of lead still had a markedly beneficial effect in retarding dezincification.

To the scientist, it was purely a matter of academic interest which of these metals, namely, tin or lead, should be added; but to the user it had a commercial interest, for there was a wide difference in cost. 50° C. was a temperature which must be commonly reached in practice in the usage of condenser tubes, especially at such points as received the first impingement of the steam; it was doubtless this fact, that certain tubes were subject to more heat than others, which accounted for selected tubes failing, whilst the remaining tubes of the installation might last for years later.

Dr. Bengough's suggestion that the range of temperature at which dezincification took place was limited required confirmation—it was certainly open to doubt whether there was any limit to this selective corrosion in the case of $70:30$ brass or Muntz's metal; and in the case of Admiralty alloy $70:29:1$ or Muntz's Nergandin brass, it was quite likely that a protective film of tin or lead was formed which prevented further action taking place. It was to be hoped that the extension of this investigation would clear this question up.

Page 60 referred to the effect of the agitation and consequent aeration of the water. The results obtained were confirmed in practice, namely, in the virulent corrosion which often took place on propeller blades, and was often found in Muntz's metal, naval brass, and manganese bronze propeller shafts, used on launches and other small craft. In such cases the abrasive action of the water must of necessity be great; nevertheless, the pitting and corrosion was not prevented, but was often aggravated. These were points of great interest.

The action of concentrated sea water did not appear to have other than a scientific interest, for its practical importance was nil; unless in the Caspian Sea, and possibly the Red Sea and the Adriatic, and in these cases the concentration would hardly reach a difference sufficient to have much importance on corrosion effect. The result of the tests in the experimental plant of the Institute of Metals at the Liverpool University went to confirm the laboratory experiments of Dr. Bengough. It was of interest to note that the Admiralty alloy tubes used contained $71\cdot18$ per cent. copper; this would in itself be in their favour in resisting dezincification; at the higher temperatures, the higher the copper contents of lead-free brass, the slower the selective corrosion. He made that statement as the result of a long series of experimental work. Otherwise the contents of the four sets of tubes were very regular and close to what was aimed at, and in every case afforded a good example of what was generally used in practice.

It was questionable whether it was altogether a misfortune that financial reasons did not permit of the running of the plant continuously

night and day and Sundays, because in marine practice it was the exception rather than the rule for condensers to run continuously over long periods. Some of the worst cases of pitting had occurred on cross-Channel and coast service vessels, and it was eminently desirable that these experiments should resemble actual service conditions as nearly as possible. With regard to the remarks on p. 70 upon temperature of circulating water, as used in the experimental plant, it was interesting to note that the temperature did not reach the 40° C. employed in the laboratory experiments, but that nevertheless some selective corrosion took place. On the renewal of the experiments it would seem to be desirable that the temperature should be allowed to reach at least 40° C. Certainly the temperatures attained in the tubes, as shown in Figs. 17, 17A, and 18 (pp. 72 and 73), were in several cases above the 50° C. line, but these tubes received the first impingement of the steam, and were scarcely a fair example. The regularity of the temperatures obtained in the four condensers was excellent, the only one of the four which showed much difference was that in which were the Muntz's metal tubes, and as this alloy was evidently not well suited for the purpose of condenser tubes the variation did not matter.

The deductions given on p. 76 were very clear and interesting.

(1) The order of dezincification put Muntz's metal and 70 : 30 brass out of count, and left Admiralty alloy 70 : 29 : 1 and Muntz's Nergandin 70 : 28 : 2 in the race.

(2) The importance of temperature and the necessity for the careful arrangement of baffle plates was certainly a point worthy of the attention of engineers and the constructors and users of condensers.

(3) Deduction No. 3 pointed to the conclusion that corrosion was *not* brought about by deposits, which were generally found on the bottom of the tubes.

(4) This deduction did away with the theory of particles being the cause of corrosion.

The protection of tubes dealt with on p. 79 was a different phase of the question of corrosion, and one which would require further investigation when the best material for condenser tubes had been finally settled. Nevertheless, there could be no question as to the efficacy of properly attached iron protection plates ; their value had been proved times innumerable in practice. Dr. Bengough's explanation of the action of this iron protection was extremely interesting, and he (Sir Gerard) thought might prove of considerable practical value.

Dealing in order with the suggestions for the prevention of corrosion on p. 87 :

(1) Water must usually be used as obtainable, and it was not often that users could be choosers. (2) It had been the aim for years of all tube makers, condenser builders, ships' engineers, and users in general, to find such a tube, but none had yet been found. (3) The adjustment of temperatures should not be difficult. Hitherto no one had attached much importance to this matter as having any bearing on the question of corrosion. The result of Dr. Bengough's investigations should change

the attitude of constructors and engineers on this subject. (4) As to electro-chemical protection, he would only say " Beware," and quote, "'Tis better to bear the ills we have, than fly to others that we know not of."

As to future experiment and practice, dealt with on p. 88, the alloys recommended in substitution of those hitherto used were Admiralty alloy 70 : 29 : 1 and Muntz's Nergandin 70 : 28 : 2. Admiralty alloy was an old acquaintance, and if well made gave a very good result (as in the case of the tubes supplied for that investigation by the Broughton Copper Company), but it was expensive. Muntz's Nergandin was a newish venture, and engineers were conservative ; it would, however, be cheaper than Admiralty alloy, and Dr. Bengough's report sufficed to show its capabilities. The chief point about it was the dissemination of the lead admixture throughout the metal—which was not quite such a simple matter as it might appear—and the use of the proper kind of copper for the purpose. It now behoved engineers to study the question of temperatures more closely, and to regulate the speed of their circulating water carefully, in addition to using the most suitable tubes. Constructors of condensers would also find much of interest in the Report, and the remarks on p. 90 were well worthy of their consideration.

In conclusion, he wished to congratulate Dr. Bengough most heartily on his work, and on his very clear and well-reasoned Report. No one who had read it could fail to realize what an immense amount of attention, time, and care must have been given to this work. He was sure that everyone, not only the members of that Institute, but also all engineers, users, builders, and shipowners ought, nay *must* be infinitely grateful to Dr. Bengough for this work, which was of world-wide value.

He would only suggest that a practical manner of showing gratitude would be to subscribe handsomely and freely to the Corrosion Fund, and thus enable Dr. Bengough to continue and to widen this research, in which he was, as the speaker knew, most deeply interested.

Professor H. C. H. CARPENTER, M.A., Ph.D. (Vice-President), said that he would like to re-echo the congratulations offered to Dr. Bengough. There was one point of great importance to which Sir Gerard had not drawn attention, and that was the fact that the results of the laboratory experiments and the large scale experiments agreed, which was an important testimony to the value of those laboratory experiments. That fact indicated that with carefully chosen conditions, even with tests on a small scale, it was possible to deduce results which would have a direct application to industrial work. Then he noticed that amongst the alloys which Dr. Bengough suggested as being possibly applicable, there were one or more copper-aluminium alloys which Mr. Edwards and he had experimented on in the eighth report to the Alloys Research Committee, and which Dr. Rosenhain tested for a longer period. He (Professor Carpenter), in conjunction with Mr. Edwards, tested them as regards corrosion under artificial conditions ; but Dr. Rosenhain tested them in the sea at Portsmouth, and those experiments went on for four years. Dr. Rosenhain

could speak on that subject with more authority; but his impression was that the general conclusion arrived at was that the rate of corrosion was extremely small. Accordingly, that series of alloys might possibly be tried in actual practice. The great difficulty was the question of production, because it was not easy to manufacture those copper alloys industrially. He did not know whether Mr. Sumner could give further information on that subject. He believed his firm had had experience with those alloys, and possibly one of the copper-aluminium alloys might be one of the solutions of that difficulty. Dr. Bengough and the Institute were very much to be congratulated on that Report, which was a most valuable piece of work.

Mr. L. Sumner, M.Sc. (Member of Council), said that he had not very much to add to what they had already heard. Sir Gerard Muntz had spoken from the manufacturer's point of view, and so did he (the speaker). He would like to congratulate Dr. Bengough on a paper which was very valuable, especially for manufacturers. The usual experience had been for the manufacturer in cases where corrosion took place to have it stated that, because the tubes had corroded, therefore the tubes were bad, and no information about the treatment the tubes had received during use was obtainable. He hoped that one effect of Dr. Bengough's Report would be that they would not receive such statements in future. He thought the conclusions that Dr. Bengough had arrived at were very largely what his firm had held for some years past, excepting where he said that particles had no effect in increasing corrosion. That supposed effect was undoubtedly one of their beliefs. Personally, he had always held the view that such particles constituted a dangerous cause of corrosion. High temperatures certainly aided corrosion a great deal, and they had also found that tubes in estuaries, or wherever there was diluted sea water, were much more liable to corrosion than when they were employed in the open sea. There was one point about the paper which he would rather like Dr. Bengough to explain, if he could. When the tubes were taken out of the experimental condenser, the top rows showed dezincification along the bottom and sides of the tubes. In the case of the middle row of tubes, dezincification appears to be also along the sides and bottoms of the tubes, but not to the same extent as in the top rows. In the bottom row of tubes, on the other hand, in the cases where dezincification does occur, this takes place on the *tops* of the tubes. He thought it would be very interesting to have Dr. Bengough's ideas—why in the bottom row of tubes the dezincification occurs on the top of the tubes, whereas in the other two rows the dezincification occurs in the sides and bottoms of the tubes. There must be some reason. In his own experience, the corrosion in actual practice was mainly along the bottom of the tubes, and it would be interesting to know why, in this particular case, the corrosion was confined to the tops of the tubes.

Another very interesting matter also related to the layer of calcium carbonate acting as a protective coating. Personally, he had always

held that this layer did form a protection against corrosion. We had all heard of, say, sister ships built at the same time, and fitted with condenser tubes manufactured at the same time. These ships traded on the same routes. Yet in one boat the tubes might fail within a comparatively short space of time, whilst the tubes of the sister boat might last a long time. He had always believed that in such cases one set of tubes were lucky enough to get a deposit which protected the tubes, whilst the other set were unlucky enough to have some corrosive action set up before they had a chance to get this protective deposit. The information given was very interesting, but the inquiry should be carried a bit further. It might be very well worth while to investigate the difference between tubes, one having a layer of calcium carbonate, and the other without it. Probably more light on the matter would thus be thrown. He did not think that Dr. Bengough was quite correct in his analysis of those tubes referred to on p. 67. He stated that in the $70:29:1$ lot there was 0.28 of lead and 0.21 of iron. He did not think that was quite correct, because the lead in tubes at the present time was only about 0.15 to 0.25 and the iron 0.07 to 0.08. Personally, he would have expected that the figures would not have come higher than the percentages he (the speaker) had just given. He noticed that Dr. Bengough had placed the copper rather high. They did endeavour to keep the copper contents of the alloy specified on the high side, as it was their belief the more zinc used the greater was the liability to corrosion.

He thought also that Dr. Bengough was rather sweeping in his condemnation of $70:30$ brass tube. When one recollected that the great bulk nowadays of the condenser tubes used in the mercantile marine were of $70:30$ mixture, and about which there was much less complaint than formerly, he hardly thought the condemnation of those tubes was warranted on the facts, and was inclined to think that the failure of the tubes might be largely due to the design of the condenser. It was necessary to keep the temperatures down, and to take care that they dealt with the proper amount of steam. He had only, in conclusion, to congratulate Dr. Bengough on his valuable paper, with which they were all very greatly impressed.

Dr. W. ROSENHAIN, B.A., F.R.S. (Member of Council), said that he could only join in the general congratulations which had already been offered to Dr. Bengough and his collaborator, and also to the Corrosion Committee as a whole on the very excellent Report which had been laid before them. There was no doubt whatever that it placed the whole of their knowledge with regard to the question of corrosion on a new basis, and on a basis which he admitted surprised him considerably, because it upset views which he thought had been universally held, particularly with regard to the influence of electrolysis. His appreciation of this work was none the less sincere, because he was not prepared to accept the Report as being quite so conclusive as some of the speakers seemed to have implied, and he fancied that Dr. Bengough in his Report had

not intended to be quite so conclusive as some of his readers appeared to have taken him to be.

He thought it was a fundamental point passed over in the paper, and rather an assumption, so far as he could judge, that pitting was due solely to dezincification. Apparently that theory was never questioned by the authors. But was that really the fact? Personally, he was inclined to doubt it. He had come across many cases, during the examination of tubes, of corrosion by pitting; but he had not in a great many cases found any trace of dezincification in the vicinity of the pits, although he had looked for it most carefully. If those cases were due to dezincification, he could only say that every particle of dezincified material had been removed before the tubes came into his hands.

The question he wanted to raise was whether there were not other forms of corrosion besides dezincification. It was said the results obtained pointed to dezincification, and not to electrolytic effect. So far so good. The information obtained was most valuable and most important, but was it exhaustive? He would point out that the experiments were on a small scale, and it was possible that with actual service condenser plant conditions were set up favourable to pitting, and this might be of the nature of localized "general" corrosion rather than localized dezincification. It was a question with him whether such results found in practice might not be due to local electrolytic action, possibly commenced through particles, spills, and so on, whose effect had not been sufficiently taken into account. It was a point of considerable importance, and he still thought it wanted proving that pitting was exclusively due to dezincification, as the paper seemed to imply.

As regarded another matter which was really only a small one, namely, the influence of temperature on dezincification, he had personally come across cases of dezincification which had occurred at ordinary temperatures, not in common sea water, but in mine waters, where the conditions were somewhat different. He had found that dezincification did occur at ordinary temperatures without any approach to 40° C. Possibly there was no controversy about that, but it might be a matter of some importance.

It was rather surprising to find that 2 per cent. of lead should apparently have such a decided protective action. While they must admit the protective effect, that effect was apparently rather against the dezincification theory. If there was such a thing as localized "general" corrosion there would be no protective action from lead. It was very important to follow out investigations in that direction, and the special laws of corrosion would have to be considered from the point of view of Sir Gerard Muntz's experiences. They could understand Sir Gerard speaking of the protective action of lead, but did it necessarily follow that because 2 per cent. of lead was protective, as Sir Gerard apparently found it, that $\frac{1}{4}$ per cent. was not injurious?

He had personally made experiments with tubes submitted to him over a good many years. He and his colleague had found that a percentage of lead up to $\frac{3}{4}$ per cent. afforded a very fair index as to how badly

the tubes would behave. They had found within this range the largest percentage of lead in the most corroded tubes in the particular specimens that had been submitted to him. He was not saying anything against the results of Dr. Bengough's experiments. From that point of view the experiments appeared to be conclusive as to the action of 2 per cent. of lead, but they would have to be very careful in deciding that question of protective action.

There had been a reference by Professor Carpenter to the resistance to corrosion of copper and aluminium, and particularly the copper-aluminium-manganese alloys. The experiments to which Professor Carpenter had referred were made in the sea at Portsmouth for two years, during which time the metal was completely immersed, and for two further years the specimens were between wind and water. At the end of that time the loss of weight was practically negligible ; whilst the surface was slightly "etched," there was no differential attack whatever. But then came the difficulty of making tubes out of those alloys. It could be done, but it was not an easy material to draw into a tube, and tube-makers would not do it unless they were obliged.

The Report would be a standby for those who had to deal with the corrosion of brass, and for others who would pursue further investigations in that direction. He personally thanked Dr. Bengough and his collaborator, and the Corrosion Committee as a whole, for the excellent record contained in that Report, and we would confidently look for further valuable work in the future.

The PRESIDENT, Professor A. K. Huntington, Assoc.R.S.M., said that there were one or two remarks he would like to make before calling upon Dr. Bengough. He had referred to drawn tubes in which, of course, the metal had had work put upon it. He might say that he himself had been for some years making experiments in other directions which had nothing to do with wrought metal or tubes, but in fact with cast metal. He used a special form of apparatus which consisted mainly of a regulated jet of sea water, regulated both as to size and force with great exactitude, and the conditions were always kept very constant. He had found in operating on metal which had been hardened on the surface by any action such as polishing that there was quite a different corrosion on the superficial layer of the metal from what took place when that superficial layer was once pierced. There was a very considerable difference directly they got through the more hardened section. It might be that the tube was sufficiently hardened already to prevent the peculiar action which he found when he pierced through the hardened skin of the polished cast metal, though it might be a question of degree rather than of kind.

As regarded dezincification at ordinary temperatures in the case of β-metal which he had specially studied, it always seemed to him that the cause of dezincification was the presence of some particle of oxide, perhaps very minute, perhaps a good deal larger, the size in fact varying very much, which formed oxychloride. This oxychloride oxidized the zinc, and, being regenerated by the sea water, continued its destructive

action. He might be wrong as to the exact *modus operandi*, but he had a very firm belief that dezincification was primarily due to the presence of minute particles, probably of oxides, which resulted in the formation of oxychlorides which brought about disaster. It was possible to look for the presence of that speck in a tube without finding it. They might not be able to see exactly what was happening, and they only got the result originating with the presence of that speck. In a casting he had detected the oxide, and watched the effects of its presence.

In the apparatus he had mentioned he worked with about two hundred gallons of sea water alternately passed between two tanks, and continuously feeding a jet under pressure which played on the piece of metal being examined. He adopted that system because he found that he could get in a short time results which would otherwise have taken him months, and possibly years, to arrive at, and it was very important that he should get those results in a reasonable time. He heated the water to about $50°$ C., and he found that that had the effect of accelerating very considerably the action of the sea water. He took it that was a rational way of hastening corrosion ; the use of acids or salts other than sea water he considered scarcely constituted a legitimate method of studying the question. It was quite rational to heat the water, and the effect of heating was to increase the rate of the attack without altering it in any way. Although Dr. Bengough did not say so, he understood him to mean in his paper that the effect was continuously increasing, and not essentially different at $40°$ or $50°$ to what it was at the ordinary temperature. They were constantly hearing expressions about metals being too pure. That expression was a little vague and required definition. They would like to know what were the particular impurities in mind when the term "impure" was used. It was quite clear they might have certain impurities present which would do harm, whilst others would do good. The somewhat loose use of that expression was probably due to their limited knowledge of the subject, and no doubt when they got more knowledge they would be able to specify much more clearly what they meant by impure, and they would be able to say that metal containing so-and-so was better than another metal which did not. That brought them to the question of electrolytic copper, which at one time had a somewhat bad reputation. There was now no doubt that a great deal of that bad reputation was due to the occlusion of sulphate of copper, which ultimately gave rise to SO_2 in the metal. That was an example of what he meant by saying that it was useless to speak about metals being pure or impure, without specifying in what the impurity consisted. At one time the electrolytic copper was supposed to be harmful because of its purity, whereas at that time it contained an' impurity which was being overlooked and was the real cause of the trouble.

Dr. Bengough, replying to the discussion, said that he would like to associate himself with Dr. Rosenhain when he practically proposed a vote of thanks to the Corrosion Committee. The work would never

have been carried out at all without the sympathetic help rendered in every possible way by the Corrosion Committee. That help was not only of a financial character, but included the giving of most useful information by the Corrosion Committee as a whole. Personally, he would have been quite at a loss how to commence the attack on the problem if he had not had behind him Sir Gerard Muntz and the members of the Corrosion Committee, all of whom had been most helpful in every possible way in enabling their investigators to carry out that work. He strongly supported that practical vote of thanks to the Committee for their share of the work.

With regard to the discussion, he found very great difficulty in replying to Sir Gerard Muntz's communication, because he had practically issued a supplementary Report, which he (Dr. Bengough) felt was really quite as valuable as the original. While Sir Gerard Muntz had had plenty of time to read through the Report, he (Dr. Bengough) was in a very disadvantageous position for dealing with his remarks. At the same time, he was very gratified indeed to find that, on the whole, Sir Gerard's practical experience showed that the work carried out in the laboratory agreed very well with what he had found in practice. He did not mean to say that that applied in every case, but generally it appeared that the explanations given in the paper did fit in with the observed facts as Sir Gerard found them. With regard to the analyses that Sir Gerard desired of the tubes sent in, it was impossible to get those. There were only two of them working, and at the particular time when most of the tubes were received he (Dr. Bengough) was single-handed. They could never have got through with other work which they regarded as more important if they had gone into all that analytical detail. They had not sufficient information of the conditions which accompanied the cases of corrosion sent in to make detailed investigations worth while in the majority of cases, and they thought it would be better to concentrate their work, in the first instance, upon experiments in which they knew the whole of the conditions, rather than spend much time on a partial investigation of such cases as those brought before their notice ; later on they would be in a better position to deal with such cases, but at first they would only use those tubes to indicate in a general way the nature of the problem. They had had over fifty tubes sent in, though they only gave the results of twenty about which they had most information ; and it would have been impossible to have kept pace with the analytical work required to investigate them all.

Sir Gerard Muntz thought that the experiments carried out at ordinary temperatures did not bear very much on the practical question of dezincification. He (Dr. Bengough) did not know that he altogether agreed with Sir Gerard in that opinion. They did not know when they started that those experiments would give negative results. They knew now that stagnant sea water at the ordinary temperature did not give rise to dezincification. Personally, in sympathy with a very large number of people, he had thought that carbon particles introduced at ordinary temperature might set up corrosion, and he had all along thought that

carbon particles might cause dezincification. Until he had investigated the matter he was persuaded that carbon particles were destructive to tubes, but he was bound to modify his opinion when he had carried out the experiments described in the Report. He thought the experiments in question had served a good purpose, even if they only gave negative results as to the causes of corrosion.

He was very much interested in the details given with regard to the annealing of Muntz's metal. Personally he had had no experience in that connection, and he was very interested, as the results dealt with not only ordinary tubes, but with different descriptions. Apparently, work had a different result on the β-phase from what it had on the a-phase. Within limits there was apparently little effect on the rate of corrosion of the a-phase, but Sir Gerard found that there was an effect on the β-phase, which they would have to bear in mind in future investigation. He presumed that the different effects obtained with annealed and unannealed β had something to do with the change to a and γ phases discovered by Professor Carpenter.

With regard to the range of temperature at which corrosion would take place, Sir Gerard rather doubted whether at higher temperatures corrosion was less effective. On that matter they must remember that oxygen in solution was absolutely necessary to corrosion, and at the boiling point there was no oxygen. It was certain, therefore, that at the boiling point there would be no corrosion, and the corrosion at temperatures slightly below the boiling point must be very small and would probably amount practically to no corrosion, but that was a point on which they wanted further investigation before they could be quite certain. He was inclined to think that at high temperatures they would find corrosion very slow. That would not affect the practical problem, because the temperature would be too high to give effective condensation.

Sir Gerard appeared to think that the experiments in the condenser plant were carried out at rather low temperatures. He (Dr. Bengough) did not quite follow the argument. In the curves given they showed that the temperature for a considerable time was well over $50°$ for the whole set of tubes, of which the results were given on page 72. In other cases they were continuously above $40°$. He did not quite follow Sir Gerard in that section of his remarks, as he thought that the experiments very well satisfied the conditions that they wanted in the condenser, especially since in the winter months the temperatures naturally fell very considerably, and they did not often get temperatures much above $38°$ or $39°$ over long periods. Possibly, he misunderstood Sir Gerard's remarks on that point, and he might be able to deal with them more satisfactorily when he saw them in print. Sir Gerard had mentioned the question of electro-chemical corrosion, and in that direction very much remained to be done. They had been gradually collecting information from users of tubes in the port of Liverpool, and he had had some very interesting results given to him in connection with the Cumberland protection process, in which a current was used. One of the biggest lines in Liverpool had obtained some very satisfactory

results, and he wanted to carry his own experiment very much further if he were permitted to do so. He thought they would be able to convince Sir Gerard Muntz that there was little danger arising from such installations if proper precautions were taken. Then with regard to the dissemination of lead in the special brass tube amounting to 2 per cent. they had examined these tubes under the microscope, and they found the lead was disseminated in a most curious and regular way. It did not occur, except to a small extent, in the middle of the α-crystal. It was in long spicules which were interwoven between the α-crystals. Finally he should like to thank Sir Gerard Muntz for his kind remarks as regards the value of the Report.

With regard to Professor Carpenter's remarks he was very glad to have Professor Carpenter's appreciation, and was especially pleased that he drew attention to the agreement between the experimental results on a small scale and the large-scale experiments. They were rather pleased at finding purely laboratory work to agree so well with the large-scale work in the special condenser, and he agreed that the use of copper and aluminium might possibly assist in the solution of the problem if manufacturers could get over the difficulty of drawing it.

With regard to Mr. Sumner's remarks, he thought they showed that his experience was in general agreement with the results shown in the Report, except in the case of particles. Mr. Sumner seemed to adhere rather strongly to the opinion that particles had an injurious effect. Well, of course, the authors of the Report could not expect the evidence in one paper would convince everybody. At the same time they thought that this matter formed a very fundamental part as regards the study of corrosion. He hoped that they would be able to add evidence to evidence until they managed to break down Mr. Sumner's scepticism on that point ; it was rather difficult to know what particles to deal with. They had dealt with all the particles they could think of, and they would be glad to try experiments with any other particles that Mr. Sumner might suggest.

With regard to the position of corrosion in tubes, he supposed that the corrosion at the sides of the tube had something to do with the general level of the water as it flowed through the tubes. That was no doubt owing to the way in which the condenser was designed. Some of the tubes were, perhaps, only partially filled with water, and the corrosion would occur at the water level. They got a greater diffusion of oxygen and a greater activity there than at the bottom of the tube. Perhaps the bottom tubes were full of water, and hot condensed water was dropping on to the outside of the top of the tube, and so heated it locally. That would account for the fact that the corrosion started at the top, and it seemed a reasonable explanation to put forward.

With regard to the analysis of the $70 : 29 : 1$ Admiralty tube he was surprised to hear Mr. Sumner expressing his doubt as to its accuracy. They would do the analysis over again, and he would take care that his printed reply should give the result of the further analysis ; but he did not think they could possibly have made such a mistake as Mr. Sumner appeared to suggest.

As regards the recommendation to abandon the use of 70 : 30 brass, of course for many purposes the 70 : 30 was all right, but the point about other tubes was that they were superior to 70 : 30 brass if they got bad conditions in the condenser. 70 : 30 brass was satisfactory under favourable conditions, but if the temperature rose or other unfavourable conditions occurred, then that alloy gave trouble. If they wanted to be quite sure of avoiding troubles they must not use that alloy for tubes which might be subjected to exceptional conditions, because there was more danger at high temperature with 70 : 30 tubes. That class of tube was satisfactory, except under adverse conditions, but these might arise at any time.

In reply to Dr. Rosenhain, he would say that he was very much obliged for his contribution to the discussion, because many of his remarks would be very stimulating, enabling them to pursue the further work which they hoped to do in the future. He quite agreed with him that all pitting was not due to dezincification. As far as the tubes sent to them were concerned they found that a large proportion were pitted in that way, and therefore they specially investigated that problem, which seemed to them the most important. In future, certainly they would devote their attention in the direction indicated by Dr. Rosenhain. He was very glad to hear that he had a large number of tubes of that kind, and he hoped he might be allowed to borrow some specimens, because they were rather badly off for tubes showing that particular form of corrosion. With regard to mining water they had not been able to tackle that, and the only water used had been sea water, and distilled water saturated with carbon dioxide, and the latter they had found to be very effective in bringing out dezincification, not in spots, but uniformly.

In trying to account for the curious action of lead in preventing dezincification, they were quite ready to admit that was a matter which required very much further work before they could say anything definite about it. He now wished to acknowledge the value of the work done by Dr. Rosenhain on the corrosion of copper-aluminium alloys. Dr. Rosenhain had carried on the work started by Professor Carpenter, and he hoped that that work would shortly be carried a stage further by himself.

The President, in his remarks, had stimulated their curiosity without entirely satisfying it. He hoped that Professor Huntington would show them a diagram of his apparatus, and let them know more about his experiments. Personally, he would be greatly interested to compare the results of the President's work with that of his own (Dr. Bengough's), and he was sure that they would be in possession of most valuable information if Professor Huntington would let them have access to his results.

The PRESIDENT remarked that he would be glad to give any information. The apparatus was worked by a petrol motor, and they made use of two hundred gallons of water, but the experiments were on cast metal, and the conditions were somewhat different.

Dr. Bengough, continuing, said he felt sure that some particulars of that apparatus would be very useful. An action which some people interpreted as erosion was very important, and took place not un- frequently at the ends of condenser tubes. The destruction was partly due to corrosion, but if they compared the President's results with those obtained in the ordinary way, they might get some very suggestive information. With regard to the particles of oxide, he could not offer any further information. Professor Huntington had suggested that the corrosion started with that oxide. They had made certain experiments bearing upon that, but they got no result whatever. They also tried zinc oxide, but he was unable to say that it was liable to start dezinci- fication in that way. He would like to know if anybody could suggest any definite particles likely to cause the reaction which the President thought would lead to dezincification. They had been unable to find anything in the way of particles liable to start dezincification. He quite agreed that until they got standardized specifications for metals they could not justifiably use the term " too pure."

In conclusion he would like to thank all those speakers who had spoken with so much kindness of the Report. He was very sorry that Mr. Jones, his collaborator, was not present to hear the discussion, and the kind words which practically every speaker had uttered about the Report itself. Mr. Jones had carried out a large part of that work, and fully deserved to share the congratulations.

The PRESIDENT said that he hoped he had their concurrence in the time they had devoted to that Report. It was the feature of the meet- ing, and he did not think that the time that had been taken over it was in any way wasted. He considered they were justified in devoting a fair amount of time to it, especially as the work which had been carried on by Dr. Bengough had been so thoroughly carried out by him practi- cally without any remuneration. It has meant an enormous amount of work and expenditure of time. That he had given freely. He therefore thought that the very least they could do was to thank him very heartily for his Report, and they could not thank him too much. He thought as time went on the undertaking of that research would do the Institute a great deal of good. They were not merely reading papers, but were actually directing investigations, which was a very important point in the carrying on of the Institute. He would not say more, but he took it they all wished to express the warmest gratitude to Dr. Bengough and appreciation of his work and the way in which he had carried it out. He would assume they signified that by their applause.

·COMMUNICATIONS.

Mr. F. A. ANDERSON, B.Sc. (Newcastle-on-Tyne), wrote that he had perused the Report with much interest, but, he confessed, with some

disappointment, for on the whole very little fresh information seemed to have been obtained, and the subject generally seemed to have been left very much where it was. It was true, however, that several facts which were very well known qualitatively—for example, the influence of temperature—had now been put on a quantitative basis as far as laboratory trials could do this, and one point in especial, the influence of small particles of carbon or other electro-negative substances in contact with the tubes, had been satisfactorily cleared up.

He doubted whether in practice only "complete corrosion" took place at ordinary temperatures—sooner or later he believed that "selective corrosion" would set in in all cases. In Table I. the cases of corrosion occurring in the "bottom section" all showed "pitting."

He was well content to notice that no novel method for the prevention of corrosion had so far been discovered as the outcome of the work, but that the electro-chemical method which had for so long been practised and recommended by his colleague, Mr. Anthony Harris, and himself, was still the most promising solution. It was also satisfactory to note that the authors clearly brought out on p. 85 an essential condition of success by that method, namely, the maintenance of a proper and effectual electrical connection between the protective masses and the surfaces to be protected. He might add that by making the connection to the blocks out of contact with water altogether, as one frequently did, the chance of losing contact here was minimized.

The condition of effectual contact, especially between tube plate and tubes, became still more important when the assistance of an external source of electrical energy was employed, otherwise that method might do more harm than good, and he and his colleague especially insisted on that in their patent No. 18,220, August 1911.

In connection with the increased tendency of the tubes to corrosion at higher temperatures, it was worth pointing out that where a protector was installed there was also an increased activity of the protector metal, and a decreased resistance of the warmer sea water, so that a larger protective current flowed. They observed in the same condenser currents 50 per cent. to 100 per cent. greater produced by blocks in the upper warmer regions as compared with those produced by their fellow blocks in the cooler portion.

He was hardly prepared to accept the theory that the efficiency of electro-chemical protection was due to the formation of a layer of calcium carbonate.

He frequently observed such deposits in laboratory experiments with tubes, but only at the end of a very considerable period, whereas a protective layer of hydrogen was doubtless formed instantly. The authors' observations, which he could corroborate, that in a laboratory trial only a momentary current flowed on closing the circuit, and that that effect could be repeated as often as desired appeared to him to be strong evidence in favour of the gas layer.

Conditions were quite different on the large scale and in a condenser in actual service. There it was found that a continuous current flowed

from the protective blocks which might amount to as much as one ampere or more per block. Doubtless the protective layer, of whatever nature it might be, was more or less continually disturbed by the flowing water.

He might add that in the case of a condenser under his immediate observation in which an independent source of current was, and is, employed, and a current of about 2 amperes per 1000 square feet passed through the tubes for considerably over a year, no appreciable deposit was found on the inside of the tubes. Laboratory tests had rather led one to fear that an inconvenient amount of internal scale would be found.

In that connection it was curious to note that the use of an electrical current from an external source had often been proposed in steam boilers for the *prevention* of scale, the theory being that the gas disengaged from the boiler surfaces would prevent the adhesion of deposits.

He could remember that suggestion certainly twenty-five years ago, and the method has been rediscovered and repatented almost annually ever since.

They welcomed the conclusions arrived at by the authors that where protective blocks were fitted, and notwithstanding that corrosive action was in evidence, the cause might be looked for in a failure in the electrical connections.

That was precisely what occurred in Case 14, Table I., when, after the protective system had been in use successfully for two years and more, corrosion of the tubes set in, through the connections becoming impaired, and was found most difficult to arrest.

It was always easier to prevent corrosion setting in than to arrest it when it had become firmly established.

Dr. C. H. Desch (Glasgow) wrote that his experience with a modification of the ferroxyl test had been similar to that of the authors. Within the last few years he had made many experiments with jelly indicators, usually with potassium ferrocyanide. In some experiments collodion had been used instead of gelatin. The results with brass and other alloys of copper had been very erratic. A strongly marked difference of potential, such as that between copper and brass, was indicated by a deposit on the anode and a pink coloration at the cathode, but local differences of composition were not indicated in this way. A piece of soft iron wire, one half of which had been struck with the hammer, showed a strongly marked difference of potential with the ferroxyl reagent, but a brass wire treated in the same manner behaved erratically, the difference being often imperceptible, and sometimes even in the reverse direction to that expected.

One of the most interesting results of the authors' important investigations was the suggestion that " complete corrosion " was entirely distinct from dezincification. The latter process could be fairly well understood, but it was very difficult to form a mental picture of the electrolytic process in the case of complete corrosion. The experiment.

showed that oxidation occurred, but did not show why copper and zinc, so different in their affinity towards oxygen, should oxidize at such a rate that there was no preferential removal of zinc from the alloy. It seemed probable that the formation of the oxide deposit took place in several stages, and that the final composition of the deposit, shown on page 29, was the result of secondary reactions. A study of the process by means of the microscope might assist in clearing up the question.

The Report marked a distinct advance in the knowledge of corrosion, and the appointment of the Committee had been fully justified.

Mr. GERALD STONEY, F.R.S. (Newcastle-on-Tyne), wrote that he had read with interest Dr. Bengough's Report of the Corrosion Committee, and noted with special interest that the alloy with 2 per cent. of lead had proved so efficient.

In the discussion at Newcastle in 1911, on Mr. Brühl's paper on " The Corrosion of Condenser Tubes," * he drew attention to the fact that there was evidence to show that old condenser tubes lasted better than modern ones, apparently owing to their not being made of pure material, and it was evident that Sir Gerard Muntz's investigations and also Dr. Bengough's bore that out. A notable point about such alloys with lead was that they were liable to be brittle about $240°$ to $250°$ C., and that had an important bearing on the use of such alloys when subjected to super-heated steam.

The fact that corrosion, especially pitting, was largely influenced by temperature was most important with regard to condensers. In a condenser the maximum temperature which any tube could attain was that due to the temperature of the steam, and it was evident from this that in a condenser with 29 inches vacuum, barometer 30, or a temperature of $26°$ C., there should be less corrosion than in one with 28 inches vacuum or $39°$ C., and still less in one with only 27 inches or 26 inches, where the temperature would be between $46°$ and $52°$ C. It therefore would be expected that the minimum corrosion should be reached in modern high vacuum condensers, and that was a further advantage in the use of high vacua apart from the gain in efficiency in the turbine or engine attached to such condensers.

With modern condensers with cooling water at about $12°$ C. there was no difficulty in getting 29 inches vacuum, and even with such a high temperature of cooling water as $25°$ C. there was no difficulty in getting 28 inches vacuum, even at rates of condensation of 12 lb. to 14 lb. of steam per square foot per hour. The rise in temperature of the cooling water depended only on the ratio between the quantity of cooling water supplied and the steam condensed, there being required approximately 560 calories to condense 1 kilogramme of steam. Thus, if the cooling water were sixty times the steam condensed, the mean rise of temperature of the cooling water would be $9°$ C., and in a good condenser the temperature of the vacuum, which was the highest temperature to which any part of the circulating water could attain, should

* *Journal of the Institute of Metals*, No. 2, 1911, vol. vi. p. 307.

not be more than 4° or 5° C. above this. In condensers which were not efficient or had been allowed to become dirty, that figure was often 12° or even more.

It was probable that much information could be got from electric power stations if the interest of the engineers there was enlisted, more especially as in many of those stations there were high vacuum condensers of modern type installed, as well as older ones with an inferior vacuum, both using the same cooling water, and it would be expected that the corrosion should be much less in the former than in the latter. Also in such stations, in many cases, records were kept of the temperatures, &c., which might be of great value, if investigated.

In further reply to the discussion the authors wrote that on seeing Dr. Rosenhain's remarks in print they felt that they should deal with them further than had been done at the meeting. Dr. Rosenhain said, " He thought it was a fundamental point passed over in the paper, and rather an assumption, so far as he could judge, that pitting was due solely to dezincification." The position of the authors in that matter was clearly stated on page 21. They said, "Complete corrosion is sometimes more pronounced at the ends of the tubes, *and may even give rise to perforation*, but this is a comparatively rare phenomenon. Usually this type of corrosion is comparatively slow, and the vast majority of tubes fail owing to pitting induced by dezincification. . . . It is, therefore, the problem of dezincification that has received the principal attention of the authors."

Since the publication of the Report a large number of cases of "failed" tubes had been sent or brought to the notice of the authors. Of such tubes 97 per cent. had failed owing to dezincification. Of the tubes examined before the Report was issued, nearly 95 per cent. had failed in the same way. (In all over 200 tubes had been examined.) Therefore they considered that they were fully justified in devoting special attention to that phenomenon, though they had realized that it was not the sole cause of trouble. On reading Dr. Rosenhain's remarks in print, they thought that he had given undue weight to that particular criticism.

In further reply to Mr. Sumner, they had had samples of the Admiralty tube re-analysed by four different workers, and the lowest result obtained by any of them was : lead, 0·24 per cent. ; iron, 0·16 per cent. Therefore they could not agree that there was any serious error in their analysis ; which error, if any, was only in the second place of decimals. They did not think that such small amounts of lead and iron would have any appreciable effect on the behaviour of the tubes towards corrosion.

They were sorry that Mr. Anderson had been disappointed with the Report, and that he considered that " on the whole very little fresh information seemed to have been obtained, and the subject generally seemed to have been left very much where it was." They might point to Sir Gerard Muntz's remark in the discussion at Ghent to the effect

that " the result of the Report was that they had to revise the whole of their preconceived theories on the subject of the action of corrosion of brass condenser tubes by sea water." They themselves did not claim as much as Sir Gerard had done for them, but they thought that, on the whole, a considerable amount of new experimental matter had been brought forward. They were inclined to agree with Mr. Anderson that selective corrosion could take place *in time* at the ordinary temperature ; practically, however, that effect did not appear to be important. They had specimens of all the standard tubes which had been immersed in sea water continuously for over a year, but none of them showed signs of dezincification, except the Muntz metal. The experiments were being continued, and possibly, given time, some of the other tubes might show dezincification, but in view of the rapidity of that selective corrosion at high temperatures, dezincification if brought about at the ordinary temperature at all became relatively unimportant.

They agreed with the views of Mr. Anderson on electro-chemical protection expressed in the next three paragraphs of his communication. They hoped in the future to convince Mr. Anderson of the importance of the calcium carbonate scale in corrosion problems. They presumed that Mr. Anderson was speaking of protective blocks of his own aluminium alloy when discussing scale formation ; their own experiments had been conducted with iron only. They agreed that corrosion was more easily prevented than stopped when it had once started.

They were much interested to hear that Dr. Desch's experience with a modification of the ferroxyl test had been similar to their own. With regard to the "complete corrosion" of brass, they had had much the same difficulty in visualizing the nature of the reaction. They thought Dr. Desch's suggestion that the oxide was formed in several stages, and that the final composition of the deposit was the result of secondary reactions, was probably the true one. They were inclined to the opinion that "dezincification" might be a slowly accumulative action—so slow that at the ordinary temperature no signs of it could be perceived in the case of the $70:30$, $70:29:1$, and $70:28:2$ tubes after 14 months' immersion in sea-water at atmospheric temperatures.

They were much obliged to Mr. Gerald Stoney for his interesting communication, which dealt with the matter from the standpoint of the engineer. In devising their scheme of further work they had paid particular attention to his remarks.

THE INTERCRYSTALLINE COHESION OF METALS *

(SECOND PAPER).

By WALTER ROSENHAIN, B.A., D.Sc., F.R.S. (MEMBER OF COUNCIL)

AND

DONALD EWEN, M.Sc.
(BOTH OF THE NATIONAL PHYSICAL LABORATORY).

IN their first paper on this subject ([1]) the present authors have put forward what they believe to be important evidence in favour of an hypothesis relating to the mechanism of inter-crystalline cohesion in metals. This hypothesis, which may be briefly termed the " amorphous cement " theory, indicates that the crystals of which metals are built up are held or " cemented " together by an extremely thin layer of amorphous or non-crystalline material chemically identical with the substance of the metal or alloy in question, but in a widely different physical state. The amorphous condition of this intercrystalline layer is regarded as being identical with or at least closely analogous to the condition of a very greatly undercooled liquid which has remained in that condition in the minute interstices which occur where adjacent crystals meet one another in various orientations.

The theory as put forward by the authors, and even the experimental evidence which they adduced in support of their view, has been subjected to a considerable and very welcome amount of criticism, and this has led the authors to carry their experimental study of the whole question considerably further, following, however, entirely different lines of reason-ing and experiment from those adopted in their previous work. In considering the value of the evidence contained both in the previous and in the present paper in regard to the support which it affords to the theory in question, it must be borne in mind that such a theory cannot, in the nature of the case, be subjected to direct experimental demon-

* Read at Autumn General Meeting, Ghent, August 29, 1913.

stration. Indeed, it is difficult to find any one line of ex-
perimental evidence which cannot be to some extent weakened
by criticism which seeks to explain the observed phenomena
in some other way which each critic for the time being
regards as more plausible. Many of these separate explanations
are in themselves difficult to sustain in the face of general
knowledge, and this difficulty becomes enormously increased
when, in order to meet the easy and simple explanation offered
by the amorphous cement theory for a whole series of pheno-
mena, it is suggested that we should accept separate and
different explanations for each set. It then becomes a question
of probability whether the one simple explanation is not more
rational and more likely to be true than a number of ways
of explaining away facts which deductive reasoning from the
theory has brought to light. As the series of such facts is
growing steadily, the case for the theory becomes correspond-
ingly stronger.

Since the publication of the authors' previous paper, the
case for the amorphous cement theory has received consider-
able support from the results of a research upon the behaviour
of iron and mild steel at high temperatures which has been
carried out by one of the present authors in conjunction with
Mr. J. C. W. Humfrey, and an account of which has been
published in the *Journal of the Iron and Steel Institute* (^{2}).
Although that research deals principally with iron, its results
are of such importance for the amorphous cement theory that
they must be briefly considered here.

The research in question dealt, among other matters, with
the mode of deformation and the mechanical properties of
very soft steel at high temperatures, and both the mechanical
tests and the microscopic observations gave results which it
would be exceedingly difficult to understand without the aid
of the amorphous cement theory. In regard to microscopic
observations the results may be summarized by saying that
while at the lower temperatures of the range investigated by
Rosenhain and Humfrey (that is, from 500° C. to 900° C.) the
strained specimens of iron exhibited much the same features
as iron strained in the cold, a very different mode of deforma-
tion became apparent at temperatures above 900° C.   Here

the development of slip-bands, which had been profuse at the lower temperatures, was very slight, and the crystals of the strained specimens showed little sign of deformation or stretching even when the test-piece as a whole had undergone large extension. On the other hand, the displacement of the intercrystal boundaries, which is comparatively slight at lower temperatures, was seen to become very large indeed above 900° C., thus leading to the conclusion that while the crystals of iron at those high temperatures had themselves undergone very little distortion, the extension of the piece as a whole had largely taken place by means of movements in the intercrystal boundaries. When such strain was carried to the point of fracture, a correspondingly striking difference was observed : where slip-bands were freely developed and the crystals were themselves elongated, the fracture showed the usual " fibrous " form, and considerable local contraction took place. Above 900° C., however, there was no local contraction, and it was clearly seen that the type of fracture was intercrystalline. Another very important factor was, however, found to enter into these phenomena, and this was the *rate* at which the strain was applied. The description just given relates to what occurs when the rate of straining is very slow or moderately slow. When rapid rates of strain are employed, however, the special features of deformation and fracture above 900° C. largely or entirely disappear—there is again marked elongation of the crystals with slip-band development, no large displacement occurs at the intercrystal boundaries, and the fracture is again of the " fibrous " type, with some reduction of area. The mechanical data confirm these differences, since it is found that rapid rates of straining lead to very much higher values for ultimate stress, the variations due to this cause amounting in some cases to several hundreds per cent. The relation between ultimate stress and rate of straining has been quantitatively determined, with the result that a parabolic law of the form $R = S^n$ has been found to connect the two factors, a law whose very form suggests the intervention of a viscous liquid in the phenomena.

The explanation of the phenomena briefly outlined above, and more fully described in the paper of Rosenhain and

Humfrey, is exceedingly simple on the amorphous cement theory. Since this same explanation also lies at the base of the experimental facts to be described in the present paper, detailed consideration may be given to it.

According to the amorphous cement theory, we have in pure or nearly pure metals an aggregate of crystals between which there is present a very thin layer of amorphous metal. In the case of a pure metal this layer will consist entirely of the pure metal itself, but in alloys its composition will be somewhat different—always, however, the amorphous layer must be regarded as a residuum of the mother-substance, whether liquid or solid, in which the existing crystals have been formed. Now as this cementing substance is assumed, by the theory, to be of the nature of greatly undercooled liquid, it must possess the properties of such a substance. What those properties are we may judge from those cases in which greatly undercooled liquids are known to us. As Tammann has shown (³), the great majority of ordinarily crystalline substances can be obtained in the form of metastable under-cooled liquid—that is, in the vitreous condition—by sufficiently rapid cooling through the freezing temperature, and he has further shown why, at temperatures very far below their freezing point, such substances show practically no tendency to undergo crystallization. Perhaps the most familiar examples of such amorphous substances are glass and vitreous silica, and their mechanical properties at temperatures some $900°$ to $1000°$ C. below their normal freezing or crystallizing point are of interest in the present connection. Such substances are very much harder and more brittle, but also much stronger than the same substance in the stable crystalline form. A glass is much harder than a felspar or a Wollastonite of the same chemical composition. Further, although they are essentially of the nature of liquids, these substances do not possess the mobility which is ordinarily associated with the term "liquid"—that is, their viscosity is very great at the ordinary temperature, but on the other hand there is still evidence that they possess the power of flowing. Thus it is well known to chemists that glass tubing, if allowed to lean against a wall at an angle, will gradually bend under its own

weight, while vitreous silica, although still harder and more viscous than glass, yet undergoes some slight amount of flow, as has been found in the course of the attempts which have been made at the National Physical Laboratory to construct a standard meter of this material ([4]). With rising temperature, however, the viscosity diminishes, slowly at first, but with increasing rapidity as the temperature rises, until at the melting point of the crystalline phase the amorphous substance reaches the same degree of fluidity as the molten material.

Bearing in mind the properties of the undercooled amorphous class of materials which have just been indicated, we may consider the effect of the presence of such a material in the intercrystalline boundaries of a crystalline aggregate. At temperatures far removed from the melting point of the crystals, the amorphous cementing layer will be harder and stronger than the material of the crystals; the intercrystal boundaries will thus be materially strengthened and stiffened by its presence, and we find, in accordance with this anticipation, that when such an aggregate is strained, deformation takes place largely within the mass of the crystals, and only comparatively slight displacement occurs at the boundaries. The relation of slip-bands to crystal boundaries at the ordinary temperature has been specially studied by Humfrey ([5]), who has found that the crystals are stiffened or supported in a very marked manner. But as the temperature is raised the relative hardness and stiffness of the amorphous material will diminish, slowly at first and very rapidly as the melting point is approached. On the other hand, there is reason to believe that the resistance of crystals to deformation by slip does not fall off very materially with rise of temperature. Diagrammatically the relative behaviour of crystals and of amorphous cement may be represented by Fig. 1, where the full curve represents the stable liquid and, at lower temperatures, the crystalline material, while the dotted curve represents the undercooled liquid. The curve AB represents the "strength" of the stable liquid phase above the melting point; the "strength" in the case of a liquid is, of course, a somewhat vague expression, since in a viscous fluid it will depend entirely upon the rate of extension. For a sufficiently slow rate of extension the "strength"—that

is, the power of resisting the applied forces—must be zero, but for a definite rate of extension the liquid must possess a definite power of resistance, and in the case of such very viscous liquids as glass or silica such "strength" is readily measured in the ordinary way. The exact shape of the curve AB and of the dotted curve BEFG will thus depend upon the rate of extension employed when the "strength" is determined—so that the term "strength" must be taken in a somewhat
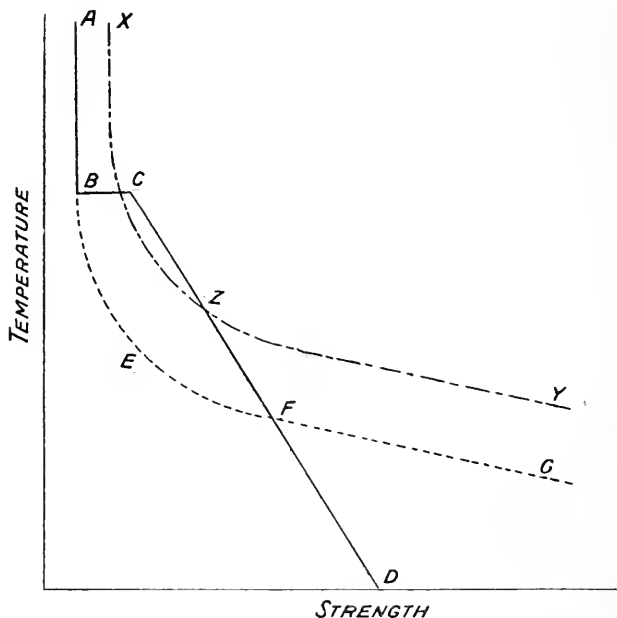

Fig. 1.

special sense. On the other hand, since the liquid, if undercooled, passes through no critical change at the freezing point (B in the diagram) the curve BEFG must be continuous with AB, and its parabolic shape is in accordance with the known (³) relationship of temperature and viscosity in many liquids. On the other hand, the crystalline phase undergoes a critical change at B, and we have therefore the discontinuity represented by BC in the strength. The line CD, which has been drawn straight for simplicity, represents the resistance to

extension of a single isolated crystal—all that is required for the present purpose is that the line CD crosses the curve BEFG—and the known relation between such substances as vitreous and crystalline silicates justifies the shape of the two curves as drawn in Fig. 1. This diagram, although admittedly largely of a qualitative nature, is yet sufficient to explain the phenomena found by Rosenhain and Humfrey and the new data presented below.

At temperatures materially below the point F, where, therefore, the intercrystalline boundaries will still be stronger than the body of the crystal, deformation will be of the ordinary or "low temperature" type, but at temperatures immediately above the point F the cementing layer in the boundaries will be weaker than the crystalline material, and there will be a strong tendency for the deformation to take place in the boundaries, while the crystals themselves remain practically free from slip. In the case of iron, investigated by Rosenhain and Humfrey, this change is particularly marked, because at a temperature which is somewhere in the neighbourhood of the point F for ordinary rates of straining the crystallized iron undergoes an allotropic transformation by which the crystals themselves become harder and stronger. The cementing material, being amorphous, does not undergo any allotropic changes, and is thus left, suddenly, much softer and weaker than the crystals. For this reason the transition from one type of deformation and fracture to the other is very marked and sudden at 900° C. in iron or soft steel; in metals free from allotropic changes the transition would be much more gradual.

The amorphous cement theory and its consequences, as indicated in the diagram of Fig. 1, thus account for the mode of deformation and fracture observed in the case of iron at temperatures above 900° C. With regard to this explanation, however, it should be added that it is not supposed that the layer of intercrystalline cement is thick enough to allow the more or less irregularly-shaped crystals to slide past one another freely; the softness of the cement merely removes the boundary support from the crystals, and deformation consequently occurs almost entirely at or near the boundaries. As a result of this deformation, fresh quantities of amorphous

material will be formed in consequence of molecular disturbance, and from the thickened amorphous layer thus temporarily formed during deformation the excess quantity will recrystallize as soon as the metal comes to rest. At the end of the straining process, therefore, we should expect to find signs of great disturbance at and near the boundaries, and the crystals should show no signs of elongation, but their boundaries will not—and indeed cannot—be the same as they were before deformation.

But not only does the diagram of Fig. 1 account for the observed results when very hot metal is slowly strained ; the effects of rapid straining are equally well accounted for. The dependence of the shape and position of the curve ABEFG upon the rate of straining has already been emphasized. If a higher rate of straining is employed, the curve will be moved to the right into some such position as that indicated by the dotted line XY crossing the line CD at Z. For temperatures between F and Z, therefore, rapid straining will result in deformation and fracture of the " low-temperature type," while slow straining will result in intercrystalline deformation and fracture.

The diagram of Fig. 1 has been employed thus far to indicate the manner in which the amorphous cement theory explains the observations of Rosenhain and Humfrey on strained γ-iron. The indications of the curve may, however, be extended in another direction, and this leads to the experimental work which forms the basis of the present paper.

The " low-temperature type " and the " high-temperature type " of *fractures*, as well as of deformation, has already been referred to in reference to iron, but it has occurred to the present authors that, in regard to the type of fracture at all events, the indications of the curves might readily be subjected to experimental verification in regard to a whole series of other metals. For it obviously follows from the diagram of Fig. 1 and the explanations already given that at temperatures above the point F (for slow straining) fracture of the intercrystalline type should result, and if the fracture is brought about at a point far enough above the point F to make the difference in power of resistance between the amorphous cement and the crystalline material large enough, not only should

the fracture be of the intercrystalline type, but it *should occur without any material deformation of the crystals themselves*, even if the crystals are those of extremely ductile metals. The exact temperature at which such a result might be anticipated will, of course, depend upon the exact shape and position of the two curves ABEFG and CD in the diagram of Fig. 1, but so long as the point F does not lie excessively close to the point C, the result indicated should be obtainable in the vicinity of the melting point. It may be said at once that the results thus anticipated from the amorphous cement theory have been obtained in a striking and satisfactory manner in the case of such typical metals as lead, tin, aluminium, and bismuth, using metal of a high degree of purity. Owing to the somewhat considerable quantities of metal required for the experiments, the more costly metals, such as pure silver and gold,* have not yet been employed, while other metals, such as copper, have been avoided, owing to the uncertainties due to oxidation at high temperatures. Some confirmatory results have also been obtained with a specially-prepared pure eutectic alloy of lead and tin.

The method of experiment which has been adopted has consisted in preparing a bar or test-piece of the metal by melting it and casting it in a suitably-shaped mould made of pure graphite. By previously warming the mould, and by regulating its rate of cooling, specimens of the desired shape could be obtained with a crystal structure whose scale could be varied to almost any desired extent, from the minute structure resulting from chilling the mould in water to test-bars consisting of one or two large crystals. The bars thus prepared were then suspended in a vertical position from a suitable support, being held by means of brass clips, and a small weight could be hung from their lower ends in order to exert a slight and constant load. The actual weight employed was about 9 lbs. for bars whose cross-sectional area was approximately 0·125 square inch, the stress employed being thus about 72 lbs. per square inch. This load was adopted because several trials with lead in particular showed that a heavier load produced fracture

* For a description of tests on gold *vide* Discussion, p. 141.

which, while still of the intercrystalline type, was accompanied by some deformation of the crystals.

The method of heating employed in the experiments consisted in raising the temperature to a point about 50° C. below the melting point of the metal in question, and holding this temperature for one hour. The loading weight was then attached, and the temperature slowly and steadily raised at a rate of about 3° C. per minute. In some of the later experiments, however, the rate of heating was considerably reduced in the vicinity of the temperature of fracture.

The central portion of each of the test-bars, which were usually cast about 7 inches long, was enclosed by a silica tube, leaving an air space of approximately $\frac{1}{8}$ inch all around the bar, and by means of a suitable winding this tube could be electrically heated to any desired temperature. Two distinct series of experiments were made, one with flat-sided bars, from which the type of fracture could be most conveniently observed and photographed, and the other with round bars, in which a protected thermocouple was embedded for the purpose of determining the exact temperature at which fracture took place under the load employed. Each metal (that is, lead, tin, bismuth, and aluminium) was tried both in the condition of fine and of coarse crystal structure, fractures being obtained of each, both in the cold and near the melting point.

The appearances of the fractures are shown in the photographs Figs. 2 to 11 inclusive. These photographs have been taken in most cases from the flat sides of the test-bars, measuring 7 inches in length by 0·5 inch in width and 0·25 inch in thickness. The bars were cast with as smooth a surface as possible, and were then etched without previous polishing. In the case of the metals with the coarser types of structure, the crystals can be distinctly seen on the etched surfaces both before and after fracture, and there is no difficulty in identifying the crystals in the vicinity of the fracture. In addition, photographs of the fracture-surfaces themselves are also given. It should perhaps be mentioned that there can be no question as to the etching process having influenced the results of these experiments, since at high temperatures unetched specimens have given the same types of

fracture as those previously etched, while at the ordinary temperature previously-etched specimens have given the same ductile fractures as unetched test-pieces.

Experiments with Lead.—Kahlbaum's pure stick lead was employed. The exact degree of purity of this material has not been determined, but it is of the same standard as that habitually employed for the standardization of thermocouples, and has been found, on careful observation, to yield a sharp and definite freezing point, thus indicating a high degree of purity.

FIG. 2.—Lead, Cold and Hot Fractures. Full size.

Fig. 2 shows, side by side, full-size photographs of two fractures of typical circular test-bars of this lead, the upper one broken at the ordinary temperature, and showing the usual high degree of ductility, with the section reduced almost to zero at the point of fracture. The lower photograph of Fig. 2, however, shows the fracture of the same material when loaded as described above, and gradually heated until fracture took place. The total absence of elongation and reduction of area is very evident, while the jagged edge of the fracture suggests its intercrystalline character. Fig. 3, Plate V., shows the appearance of a fracture similar to that of the lower photograph in Fig. 2, but taken from a bar of square cross-section having a fairly small crystal structure. The photograph shows the fractured surface under a magnification of 3 diameters, and the individual crystals radiating inwards

I

from the outside surfaces of the bar are very clearly shown. This fracture recalls that of a piece of cast steel or other hard metal rather than that of pure lead.   A coarsely-crystalline bar of the same lead gave a strikingly intercrystalline fracture, but owing to the rapidity with which etched lead tarnishes it has not been possible to take a satisfactory photograph showing the relation of the fracture to the crystalline structure as existing before fracture.   The specimens themselves, however, are entirely convincing.

Experiments with Tin.—The material employed was Kahlbaum stick tin, and the remarks made above with regard to the purity of the lead also apply to this material.   As even " commercially pure " tin is a particularly pure material, the metal employed in the present experiments is probably very pure indeed.   The behaviour of this material when broken at a high temperature in the form of bars of rectangular cross-section is illustrated by the photographs of Fig. 4, Plate I., which show the structure of the bar before straining and after it had been broken, magnified two diameters.   The lighting of the specimen in the two cases is very slightly different, and this makes the relative brightness of some of the crystals somewhat different in the two photographs taken before and after fracture, but the same crystals can readily be identified in both.

The exact manner in which the fracture follows the crystal boundaries is very clearly seen in the specimen ; in the photograph Fig. 4*b*, Plate I., the true edge of the fracture is somewhat obscured by the slightly out-of-focus image of the sloping surfaces of the fracture itself which lie behind the plane of the etched surface of the bar.   In order to overcome this difficulty, a second photograph of the fractured specimen is given in Fig. 4*c*, Plate I., and in this the true edge of the fracture has been made more obvious by carefully and accurately blocking out the interfering indistinct images.   The blocking-out has been controlled by careful comparison with the specimen itself.   Similar blocking-out has, for the sake of clearness, been resorted to in Figs. 6, 7, 8, and 10.   As the specimens themselves will be available for inspection, the authors regard it as unnecessary to reproduce these figures in duplicate in the manner which has been employed in the case of Figs. 4*b* and *c*.

The fact that the crystals have undergone no appreciable deformation is also illustrated by these photographs. Fig. 5, Plate V., shows a portion of another fracture of tin at a temperature near its melting point, but the higher magnification in this case (11 diameters) makes the pulling apart of the crystals along their boundaries very plain. It may be mentioned that Fig. 5, Plate V., is the only photograph in the present paper taken under vertical illumination. Finally, Fig. 6, Plate II., shows two fractures of rectangular bars of tin, the upper one broken while hot and the other broken in the cold, both magnified two diameters. The crystal size of both specimens is equally large, but the piece broken in the cold shows the elongation of the crystals, the local contraction at the fracture and the cleavage-fracture running across the crystals and not along their boundaries, these being typical of normal fractures.

Experiments with Aluminium.—These were conducted on the same lines as those described in the case of tin, but the material in this case was rather less pure, being simply the purest form of aluminium obtainable commercially and containing approximately 99·7 per cent. of aluminium. Only one photograph is given, Fig. 7, Plate II., which shows the intercrystalline fracture, unaccompanied by distortion, which is obtained when this metal is broken under a low load near its melting point.

Experiments with Bismuth.—Bismuth was chosen as a typical brittle metal in contrast to the very soft and ductile ones previously dealt with. In this case the fracture in the cold could not, of course, show any elongation of the crystals or reduction of area, but it did show very clearly that the brittle fracture in the cold takes place along the cleavages of the crystals and not along the intercrystal boundaries. The fracture at a temperature near the melting point, however, exhibits the same features as have already been described for the other metals, except that—owing to the great brittleness of the crystals themselves—a few fragments have become detached at the moment of fracture. Fig. 8, Plate III., shows the same bar of bismuth before and after fracture at a high temperature, and it will be seen that the photographs illustrate the same features as in the case of tin and aluminium. The contrast

between the two types of fracture, as obtained at the ordinary
temperature and near the melting point, is best illustrated by
an examination of the fractured surfaces themselves.   These
are seen side by side in the two photographs of Fig. 9, Plate III.,
magnified two diameters.   The right-hand photograph illus-
trates the typical cleavage fracture obtained at the ordinary
temperature—the flat cleavage faces of the broken crystals are
plainly seen in the figure.   On the left-hand side is shown
the typical high-temperature fracture of a portion of the same
bar of bismuth.   This fracture is a particularly difficult sub-
ject to photograph, and the picture—while it serves to show
the marked difference between the two types of fracture—
does not make the intercrystalline nature of the hot fracture
nearly so evident as does an inspection of the specimen itself;
the absence of the flat cleavage surfaces and of the typical
lines and markings of such faces in bismuth is, however,
evident even on the photograph.

The experiments already described show definitely that at
some temperature below the melting point of the metal, bars
of certain pure metals undergo fracture under a very mode-
rate stress by the separation of the crystals from one another
along their boundaries and without any appreciable distortion
of the crystals themselves.   Incidentally it may be remarked
that the general fact that all metals become extremely weak
and brittle at temperatures near their melting points has long
been known and is utilized in certain industrial processes; so
far as the authors are aware, however, the nature or mechan-
ism of this brittleness was not known, and it has remained
for the amorphous cement theory to lead to the prediction
that at temperatures near their melting points metals would
exhibit brittleness of an intercrystalline character.

In order to determine the exact temperature at which
these brittle intercrystalline fractures occur, a special series
of experiments was undertaken.   A first attempt to determine
the temperature of the test-bars in these experiments by
lashing a thermocouple against their surface was soon found
to give unsatisfactory results, probably because the thermo-
couple in such circumstances is always somewhat hotter than
the mass of the metal.   An attempt was next made to

prepare test-bars, or rather ingots, of a tubular form, so that the thermocouple could be introduced into the centre of the bar. It was, however, found very difficult to make such castings, and only in one case, working with lead, was the attempt successful. The method ultimately adopted was to insert into one end of the mould a very thin tube of vitreous silica closed at one end. The metal was allowed to solidify around this tube, and a thermocouple was then inserted into this central tube in such a way as to measure the temperature of that part of the bar which was placed in the hottest part of the heating tube during the experiment. Unfortunately, fracture did not always take place exactly at the end of the silica tube where the thermocouple was situated, and the temperatures given by that means are therefore rather maximum values—the actual fractures probably took place at points in the metal a few degrees (possibly 3 or 4) lower than the temperature indicated. With this reservation, the temperatures at which fracture of the brittle intercrystalline type took place under a load that was not large enough to cause material elongation of the specimens is given in the following table :—

Temperature of Brittle Intercrystalline Fracture.

Metal.	Condition.	Position of Thermocouple.	Temperature, Degrees C.	Freezing Point, Degrees C.
Lead	Small crystals	In silica tube	323	327
Lead	,, ,,	Tubular ingot	324	327
Tin	...	Couple $\frac{1}{2}$ inch from fracture	223	232
Bismuth	Small crystals	Couple $\frac{1}{4}$ inch from fracture	261	268
Aluminium	,, ,,	Couple $\frac{3}{8}$ inch from fracture	637	657

For purposes of comparison, the freezing points of the same metals as determined with the same thermocouples are given in the last column of the table. It will be seen that although in the case of lead the brittle fracture is obtained at a temperature only 3° C. below the freezing point, yet the differences between the observed temperatures of fracture and the actual melting points are in every case well beyond the limits of experimental error. In a few cases, particularly

with lead, signs of fusion were visible near the corners of the
broken test-pieces, but with the other metals this was not the
case, and the mere fact that the fractures shown in the photo-
graphs have been obtained at all serves to prove that the
phenomenon occurs at a temperature below that at which the
metal begins to melt, otherwise sharp-edged fractures could
not have been obtained.

Although the phenomena of intercrystalline brittleness at
temperatures just below the melting point were first sought
for because their existence had been predicted from the
amorphous cement theory, and the authors therefore regard
their observations as strongly supporting that theory, it is yet
necessary to consider whether any other explanation of these
phenomena can be given. At least one such alternative
explanation suggests itself at once, and deserves careful
consideration ; this is the view that the phenomena may be
due to the presence of fusible impurities or eutectics in the
intercrystal boundaries even of a " pure " metal.   There
are, however, difficulties in the way of that explanation which
the authors regard as conclusive.

In the first place, the metals employed by the authors for
their experiments are of a high degree of purity—so high,
indeed, that it would probably have been necessary to develop
special methods of analysis in order to determine the true
quantities of the " traces " of impurities which are present in
these materials.   Admitting that there may be very small
but appreciable quantities of impurity present even in the
purest metals obtainable, the question arises, in what form or
condition such impurities will exist.   If they are capable of
dissolving in the metal when the latter is fluid, we may expect
to find them present either in solid solution or, it may be
suggested, in the form of very thin films of " eutectic " in the
intercrystalline boundaries.   If they are present in the form
of solid solution. then they will not be very greatly con-
centrated (if at all) in or near the crystal boundaries, and
therefore cannot play any part in the phenomena under
discussion.   Now it is admitted that there must be some
small degree of mutual solubility in the solid state between
any two substances, and it therefore follows that in very pure

metals all the impurities present must be held in the state of solid solution. But even if we suppose that the solubility of one of these impurities is so small that even the minute quantity present in the metal cannot be retained in solid solution, it does not follow that the foreign substance in question can be present as a eutectic at all, and still less as a continuous intercrystalline film. In the first place, only a few even of the metallic impurities likely to be present in these metals are capable of forming a eutectic. Taking the case of lead, the impurities likely to be found are antimony, copper, iron, silver, zinc, and, very rarely even in commercial lead, nickel and bismuth. Of these only four—antimony, zinc, silver, and bismuth—form eutectic alloys, and before these could form a film which could affect the phenomena, they would have to be present in a sufficient quantity. What is this quantity ? The answer may be sought by studying the structure of known alloys of lead with other metals, and of these the lead-tin system has been most carefully studied ([6]). Reference to the photomicrographs illustrating the paper of Rosenhain and Tucker on this series will show that when the eutectic alloy first makes its appearance at the tin end of the series, the proportion of lead present is of the order of 1 per cent., and at that concentration the eutectic does not form continuous cell-walls, but lies in short streaks and patches ; a concentration of 2 per cent. of lead is required before a sufficient eutectic network is formed to affect the mode of fracture. At the lead end of this series a concentration of over 16 per cent. of tin is required before eutectic appears, and it is most probable that the solubility of many other metals in solid lead is of the same order of magnitude. Still, even in the total absence of solid solubility, it would seem that a concentration of about 2 per cent. of the eutectic-forming body would be required to yield a network approaching sufficiently near to continuity to produce an apparently intercrystalline fracture when the eutectic had been melted by heat. In the case of lead and tin, the " eutectic-forming body " would in the case of nearly every metallic impurity be the foreign metal as such, but where inter-metallic compounds exist and act as eutectic-forming bodies, the concentration

required might be only of the order of 2 per cent. of the compound, and this might reduce the necessary concentration of the foreign metal to the order of 0·2 per cent. Even this quantity, however, is certainly not present in the pure varieties of lead and tin which have been employed by the authors in the present experiments.

It might, of course, be suggested that although microscopically visible eutectic films do not appear until a fairly high concentration of impurity is present, ultra-microscopic films may exist even when no eutectic at all is visible. This is, of course, at best a theoretical assumption of the same order as the authors' hypothesis of an amorphous cement, and can only be judged upon its merits as regards probability. From this point of view its position is, however, very weak, since it is well known that such bodies as eutectics tend to segregate or " ball up " under suitable conditions ; when eutectic is present in minute traces only it is never seen—in slowly-cooled or well-annealed alloys—in the form of thin films or layers but always in rounded masses. Indeed, the forms assumed by eutectics are of such a character as to indicate that surface-tension forces have been powerful factors in determining the resulting shapes, and the existence of extremely attenuated films cannot be reconciled with such actions of surface-tension, which would cause these films to draw together into minute globules. In the authors' experiments with coarsely-crystalline metals the rate of solidification was extremely slow, so that any eutectics present would have had ample time to coalesce into globules ; in such very slowly cooled metal the existence of thin eutectic films is hardly possible, and yet their behaviour in regard to intercrystalline brittleness at high temperatures is quite as striking as that of chilled metal.

Finally, however, the " eutectic film " explanation meets with another objection which can hardly be surmounted. All the known eutectic alloys into which lead and tin can enter have a melting point which is not 10° or 20° lower than that of the pure metal, but of the order of at least 100° lower. If, therefore, the fusion of thin intercrystalline eutectic films were at the root of the intercrystal brittleness

PLATE I

FIG. 4 (a).   FIG. 4 (b).   FIG. 4 (c).

PLATE II
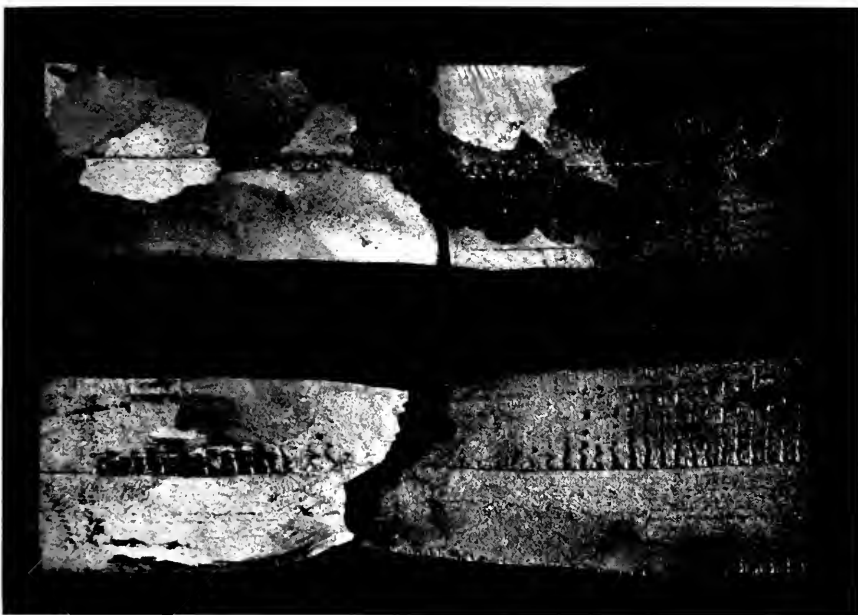
FIG. 6.—Tin, Cold and Hot Fractures.
Magnified 2 diameters.
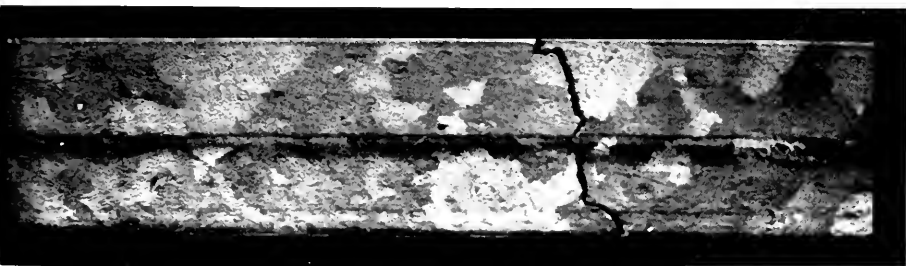
FIG. 7.—Aluminium, Hot Fracture.
Magnified 2 diameters.

PLATE III

FIG. 8.—Strip of Bismuth, before and after Fracture.
Slightly magnified.

FIG. 9.—Bismuth, Hot and Cold Fractures.
Magnified 2 diameters.

PLATE IV
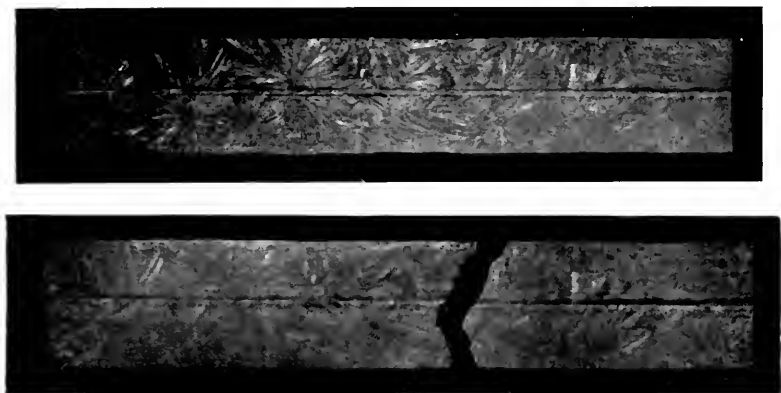
FIG. 10.—Lead-tin Eutectic Alloy before and after Breaking.
Slightly magnified.
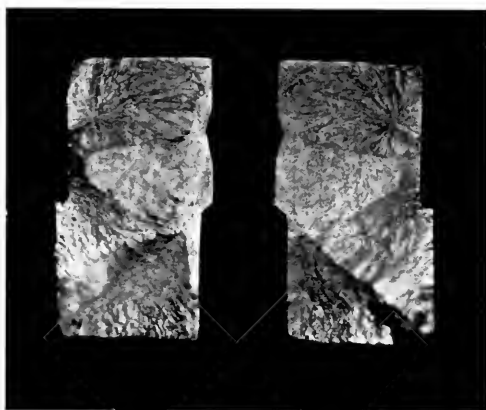
FIG. 11.—Lead-tin Eutectic Alloy, Hot Fracture.
Magnified 3 diameters.

PLATE V
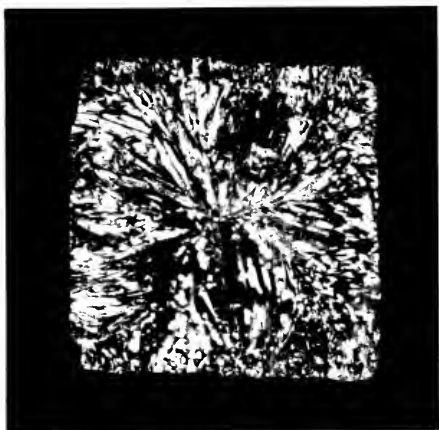
FIG. 3.—Lead, Hot Fracture.
Magnified 3 diameters.
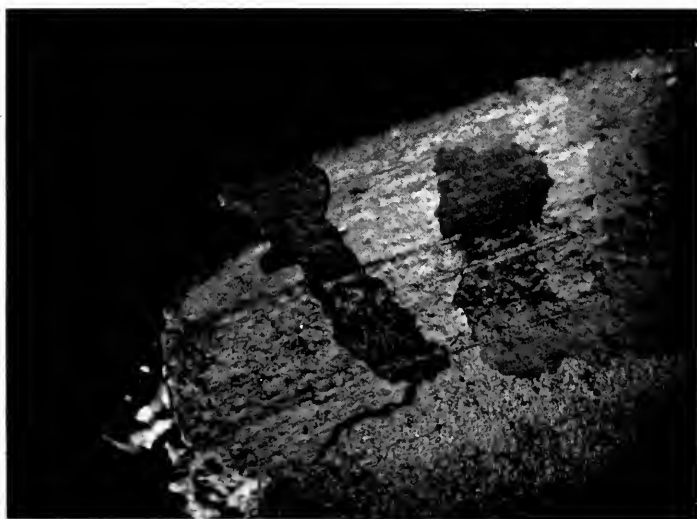
FIG. 5.—Tin, showing Intercrystalline Fracture.
Magnified 11 diameters.

observed by the authors, that brittleness should be met at the temperatures at which these eutectics become fluid— that is, $100°$ or more below the melting point of the metal, and not only a few degrees below that melting point.

On this last ground alone, the authors feel satisfied that the " eutectic film " explanation must be dismissed as untenable, but in order to dispose of this view still more effectually they have tried to extend their experiments on intercrystal brittleness near the melting point to an actual eutectic alloy, choosing for their experiment one with which they are specially familiar, viz. the eutectic alloy of lead and tin.   Before describing this experiment it will be well to consider what the amorphous cement theory would lead one to anticipate in dealing with a eutectic alloy.   It has been shown by Rosenhain and Tucker [6], and the view has since been amplified by Guertler [7], that eutectic alloys, like pure metals, consist of crystal grains, but that each crystal grain of such a eutectic is really a skeleton crystal of one of the two constituents, which may be termed the " predominant partner " in the eutectic—the interstices of this skeleton crystal being filled in by lamellar crystals of the other metal.   In a eutectic alloy, therefore, there are two types of " crystal boundaries "— viz. the larger boundaries surrounding the grains and the boundaries between the lamellæ within each grain.   Now in the case of the lead-tin eutectic even at the ordinary temperature we are not very far removed from the melting point, and it is possible that we are above the point corresponding to F in the diagram of Fig. 1.   In that case we should expect to find that when a polished specimen of this eutectic is strained, movement should occur chiefly along the crystal boundaries of both types mentioned above.   That this is actually the case has been shown by Ewing and Rosenhain in 1899 [8], but the reason for this phenomenon has remained unrecognized until the advent of the amorphous cement theory, which now offers a simple and satisfactory explanation.

With this form of behaviour under strain in mind, it will be clear that " intercrystal " fracture in accordance with the amorphous cement theory might occur in a eutectic in two

ways—either between the larger grains, or between the fine
lamellæ within the grains.   The only really characteristic
feature to be looked for with certainty, therefore, is a very
brittle fracture without elongation of the grains.   On the
other hand, fracture will usually follow the shortest available
path, and for that reason we should expect that in favourable
circumstances a bar of eutectic alloy might be caused to
break by separation of the comparatively large grains.   The
authors' experiments with the lead-tin eutectic have entirely
confirmed these expectations ; when treated in the same
manner as the bars of pure metal—that is, by gradual heat-
ing under a small load—brittle fracture results, and in favour-
able circumstances examples of intergranular fracture have
been obtained.

These fractures are illustrated in Figs. 10 and 11, Plate IV.
In the former the short jagged fracture of a bar of the lead-tin
eutectic is shown a little larger than full size.   The spheru-
litic crystal grains of the eutectic structure are only faintly
shown, but the detailed microscopic examination of the speci-
men shows that this brittle fracture shows *both* types indicated
above, the fracture being partly intergranular and partly inter-
lamellar.   The photographs of the fractured surface in Fig. 11
(magnified 3 diameters) show these two types more clearly ;
the two photographs show the two halves of the fracture.   In
the upper portion of each is seen the interlamellar fracture
of one large grain, where the spherulitic arrangement of the
lamellæ is distinctly seen ; the lower portions on the other
hand show the typical features of intergranular fracture.

The only real difference between the behaviour of the
eutectic and of the pure metals lies in the temperature at
which fracture occurs.   In the pure metals the interval
between the temperature of fracture and the melting point
was never found to be less than $3°$ C., but with the lead-tin
eutectic the corresponding interval — carefully determined
with a specially sensitive thermocouple and instrument—
was found to be only $0·5°$ C.

The object of the experiment with the eutectic alloy—
apart from its intrinsic interest—was to show that when the
intervention of a eutectic is to a large extent eliminated, the

same type of phenomena still exist. Of course it still remains possible to suggest that there are yet more fusible films due to other impurities between the eutectic grains, but beyond the serious objections to such an explanation which have already been indicated, there is the added fact that in order to lower the freezing point of these films below that of the eutectic, impurities of a very special nature would be required, since only a few special elements enter into the formation of highly-fusible ternary and quaternary eutectics. The probability of the explanation on these grounds is therefore enormously diminished in the case of the experiment conducted with the eutectic alloy.

In the present paper the authors have endeavoured to bring forward some additional evidence in support of the " amorphous cement " theory. The fact that the brittleness of metals at high temperatures is due to intercrystalline weakness has been clearly demonstrated, and it has been shown how this experimental fact has been arrived at as a result of prediction from the theory in question. As the power of predicting and guiding to the discovery of new facts is generally regarded as the best test of the truth and value of any theory, the authors feel that the case for the " amorphous cement" theory has now been materially strengthened. There are, however, a number of other directions in which that theory has suggested and is suggesting new lines of experimental inquiry which the authors hope to follow up. Meanwhile they will welcome the most critical discussion of their views.

The experiments described in the present paper have been carried out in the Metallurgical Department of the National Physical Laboratory, and the authors desire to express their indebtedness to Dr. R. T. Glazebrook, C.B., F.R.S., Director of the Laboratory.

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DISCUSSION.

Dr. ROSENHAIN, in introducing the paper, gave a brief account of the principal contents. In addition to the data contained in the paper, however, he said that he was able to show the meeting the results of more recent experiments than any of those described in the text ; he referred to the fracture of a small bar of extremely pure gold at a temperature a few degrees below its melting point. The gold had been lent to the National Physical Laboratory for the purpose of this research by the courtesy of the Deputy Master of the Royal Mint and of Dr. T. K. Rose, Chief Chemist and Assayer to the Royal Mint. By the kindness of the latter gentleman the gold had been prepared of a very exceptional degree of purity; in fact, Dr. Rose had assured him that the sample was one of the purest specimens of metal which had ever been produced. The gold had been sent to the National Physical Laboratory in the form of sheet, and had been remelted by them in an electrically heated resistance furnace, the gold being contained in a vessel of pure graphite. Any contamination that might occur in that process was obviously extremely slight, and the fractured bar might therefore be taken as representing the purest metal experimentally obtainable. Dr. Rosenhain exhibited the broken bar of gold, which showed features of brittle intercrystalline fracture identical with those described for other metals in the body of the paper. He drew attention to the fact that this result strongly confirmed the view expressed in the paper, that impurities did not play a material part in the phenomena described.

Dr. T. K. ROSE (London) said that the paper interested him very much, and he was not in the least disposed to doubt the well-grounded theory which Dr. Rosenhain had put forward. In this paper Dr. Rosenhain had put forward, as the chief piece of evidence in favour of the theory, the breaking of the metal two or three degrees below its melting point. Dr. Rosenhain told them that, in measuring the temperature, he began by putting the pyrometer outside the piece of metal, and ended by placing it in its centre. This would be the last place heated, and with moderately rapid heating might be $2°$ or $3°$ below the temperature of the bulk of the metal. The old belief was that the intercrystalline spaces were really spaces with interlocking crystals, and these crystals, projecting into the intercrystalline spaces, might melt first, just as the projecting burrs on a piece of metal melt first, with the result that the intercrystalline spaces would offer no resistance to rupture, and the results obtained by Dr. Rosenhain might be expected to occur.

He would say a word as to the pure gold used by Dr. Rosenhain. It was a piece of the No. 8 plate mentioned in his (the speaker's) paper on Annealing, and was at least equal in purity to any specimen which had come into his hands. Among other precautions which he had taken in its preparation, the precipitated gold, after washing and drying, had been melted *in vacuo* in a quartz vessel, and allowed to cool before air was admitted. The metal had not been cast at all.

Dr. W. GUERTLER (Berlin) said that Dr. Rosenhain's paper was a remarkable one, and that it dealt with a very important subject. It was not yet sufficiently appreciated how much more the mechanical properties of metals and alloys depended upon their treatment and upon their structure than upon their chemical composition. It has, for instance, only lately become known that it was possible to produce a ductile condition with very brittle stuff if it were brought into the right structure, and that one could influence those qualities more by mechanical and thermal treatment than by chemical additions.

The most important points that Dr. Rosenhain had called attention to were the influences of temperature. Dr. Bengough's paper, when first published, showed how the mechanical properties changed in accordance with changes of temperature in a very astonishing manner, which at first seemed quite unexplainable. The phenomena were apparently independent of the chemical composition, and were brought about solely by changes of temperature. The curves had all the same shape, whether copper, nickel, or brass, or some similar metal, was taken. There was no possibility of explaining this until one came to that special research on the intercrystalline boundaries.

The other important point in mechanical testing was the influence of time. Nearly all the tests given in the literature gave the figures, without any notes, as to the time of loading and so forth, and of course that led to great mistakes and great uncertainty; but the case was not as bad as it might have been, because, as Dr. Rosenhain showed, the percentage of change which it was possible to bring in by varying the temperature of loading was very much less at low temperatures than at high temperatures, and on approaching the melting point the influence of time could render the results very fluctuating. He (Dr. Guertler) thought that the facts were clearly stated, but that there was some doubt about the theoretical explanation in regard to the idea of metals being in an amorphous state so far below the melting point. Dr. Guertler said that the change from the amorphous to the crystalline state was enormously rapid in all the metals and alloys, and that they could not be kept in an amorphous state under other conditions. He understood that Dr. Rosenhain stated that the amorphous parts were at first in the form of a thin layer of a thickness of one molecule——

Dr. ROSENHAIN, interrupting, said he could not accept that, as such a thickness would be of no use.

Dr. GUERTLER, continuing, said that he quite agreed with Dr. Rosenhain in thinking that the very slight thickness of the amorphous layer could not explain all the observed phenomena, but that he could not believe in the existence of an amorphous state unless it be confined to the thickness of one molecule. The crystals came very near to each other, leaving only a very narrow space between them, where the closest possible packing of the molecules was discontinued, and where there might be molecules which could not find space to fit into one or the

other crystal ; but so long as that amorphous theory confined itself to the supposition of these molecules which could not find any crystalline adjustment, and therefore might be called amorphous, he entirely agreed, and he thought that, so far, it was a wonderful way of explaining many changes of properties with temperature. However, he still thought that the obvious irregularities which Dr. Bengough and some others had called attention to required additional explanation. Not everything could be explained by that theory, excellent though it might be. Dr. Rosenhain himself dealt with the question of the impurities, and it might be that the impurities were between the crystals, and therefore they were more likely to break than the crystals themselves. But Dr. Rosenhain said that those impurities were so small in amount that they would be taken up in solid solution. He (Dr. Guertler) did not think that was neces-sarily the case. Especially if one took, for example, bismuth and added only 0·1 per cent. of oxygen, then the oxygen would make 1 per cent. of oxide, and 1 per cent. of oxide would make a good eutectic. He had at home a sample of lead containing less than 1 per thousand of oxygen, and in the structure of the polished specimen one could see the impurity in the form of long needles in the mass of the lead. This amount of oxide could not be found analytically. Similar conditions might prevail where arsenic was used. Dr. Rosenhain had said that those little impurities, if they were present, must assume the form of eutectics which would melt at something like 60° below the melting point of pure metal. He (Dr. Guertler) would draw attention to the fact that there were a number of eutectics which melted at points only a few degrees below the melting point of the pure metal. If all the impurity were taken up in solid solution and no eutectic were present, the soften-ing would start below the melting point of the pure metal when at some intermediate point between that and the eutectic point the solidus curve was passed. Taking into consideration the totality of the different impurities which might be present, one would perceive that those eutectics, or points of the solidus curve, were passed one after the other, which gradually would loosen the cohesion. He thought one would have to consider that point as an additional theory to explain some of the irregularities which could not be explained alone by Dr. Rosenhain's amorphous theory.

Captain N. T. BELAIEW (St. Petersburg) said that he offered his con-gratulations to Dr. Rosenhain on his very valuable paper. He wished to know whether the well-known phenomena of recrystallization could be satisfactorily explained by Dr. Rosenhain's theory. They knew that the interstices in iron grains would grow greater and greater at about a certain temperature. He would like to know if, during the growing process, the inlayer of the amorphous material was still in existence.

Professor S. L. HOYT (Minnesota) said that he would like to say a word or two about Fig. 1 on p. 124, and especially about the line AEFG. That line was supposed to show the relation between strength

and temperature in amorphous substances. They knew that the degree
of viscosity was very dependent on temperature, but if they looked at
that curve they would see that as the temperature decreased the rate at
which the strength increased, increased very rapidly. That was really just
opposite to what actually did take place. He believed that the whole
paper would be increased in strength if experiments were actually
carried out in a like manner for the purpose of showing the behaviour
of amorphous substances. Take, for example, wax or glass. With
those substances they could find out if there were some critical point
the same as they found in the case of pure metals. Dr. Rosenhain
made a statement also that if a large weight were suspended on the
bars, the metal would pull out before the cement had a chance to
break. If there were a layer of greater than molecular dimensions
between the crystals, would that be so dependent upon the actual
weight? Personally, he could not see that it was.

Mr. E. L. RHEAD, M.Sc.Tech. (Manchester), said he would like to
know whether Dr. Rosenhain had taken into consideration the possibility
of different expansions occurring in different directions in the crystal
grains, as by raising the temperatures they might reduce the density
of the material, and so that would lead to immediate fracture.

Dr. ROSENHAIN, in replying to the Discussion, said that he would not
attempt to deal in detail with the whole of the points raised, but only
with two or three which were of special interest, because they appear
to be adverse to the theory advanced by him.

Dr. Rose raised the question whether the authors really knew that
the temperatures of fracture were actually below the melting point. In
reply to that query, he would ask Dr. Rose to examine the fractures,
and to notice the sharp edges where the metal had broken off. If the
temperature had not really been below the melting point, such sharpness
would have been impossible; all the edges would have been rounded.
That alone was sufficient to show that the specimens had been broken
at a temperature definitely below the melting point. Further, there was
every reason to believe that the temperatures indicated by the thermo-
couples and quoted in the paper were on the high side, and in many
cases the temperature differences observed were distinctly larger than
any experimental error.

Dr. Rose had then suggested a possible alternative explanation of
the phenomena; but even assuming that the strength properties of the
metal at the ordinary temperature could be accounted for by the inter-
locking projections of which Dr. Rose had spoken, it was yet difficult
to see why those projections should melt first. It was true that pro-
jections on the outside piece of metal which was being heated from the
outside would melt first, but that was because those projections received
the heat and attained the melting temperature earlier than the bulk of
the metal. Interlocking projections on an internal crystal boundary,
however, would not be situated in a corresponding way; if these were

to melt first we would have to assume, on the theory indicated by Dr. Rose, that the heat reached these internal projections sooner than it reached the bulk of the metal. This would imply that the heat travelled along the crystal boundaries more easily and more rapidly than through the bulk of the metal. Now, on the interlocking projection theory, the boundaries consisted of spaces filled with air or other gases, and it was obviously impossible to believe that these would conduct the heat more rapidly than the metal itself.

Turning to Dr. Guertler's criticisms, he (Dr. Rosenhain) was not prepared to accept the view that an intercrystalline layer of amorphous cement should be only one molecule in thickness. Both the mechanical strength of the boundaries at the ordinary temperature and their viscous behaviour at high temperatures required a layer of much more substantial thickness. On the other hand, the whole point turned on the question of what we were to understand by the term "molecule" in this connection. The molecules of which the crystals were built might be many times larger than the molecule of the liquid phase, but to account for the observed facts Dr. Rosenhain thought that the amorphous layer would have to be several times as thick as the "liquid" molecule.

With regard to the suggestion that minute traces of impurity, although present in solid solution, would segregate in the boundaries and result in the formation of a liquid film at the temperature of the solidus, he would point out that this process of segregation was one of outward diffusion from the mass of the crystals to the boundaries, and was consequently very slow. Those who have undertaken experiments for determining the solidus by quenching know that, even in an alloy having a very minute structure, the time required for this process was several hours, even where the quantity of the impurity or foreign metal was considerable. In the experiments described in the present paper the quantity of impurity was extremely small, while in many cases the crystal structure was enormously large compared with those met with in the quenching experiments just referred to. It would seem, therefore, that the process of outward diffusion required by Dr. Guertler's suggestion might occupy days and even weeks; it could hardly enter into the experiments described in the paper which were completed in minutes rather than hours.

In reply to Professor Hoyt, he (Dr. Rosenhain) quite agreed that the diagram given in the paper would not correctly represent the properties of glass at temperatures below 100° C., but the diagram was not drawn for the purpose of representing those properties, and he thought that if Professor Hoyt had read the paper a little more carefully, he would not have endeavoured to test the reasonableness of the diagram by stretching its interpretation in this way. On the other hand, the experimental study of glass or other highly undercooled liquids might be interesting; but the continuous manner in which the properties of glass changed from the ordinary temperature right up to that of complete fusion rendered it quite certain that the tensile strength also would change in that way. Different undercooled liquids would no doubt differ in

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the precise position of the curves representing their strength, but one could not anticipate any radical change of shape. In any case it would be no sounder to argue from undercooled glass to undercooled metal than it was to argue from undercooled organic liquids.

The manner in which the amorphous cement theory lent itself to the explanation of the phenomena of annealing had been dealt with by him elsewhere.* The theory indicated that the amorphous film would persist throughout the whole process of annealing and recrystallization. Mr. Rhead had suggested the influence of different degrees of expansion in different directions in the crystals of the metal. Certain phenomena, known as "heat reliefs," had been observed and studied, which were generally ascribed to the influence of these different expansions ; but anyone who had observed these phenomena would realize that the displacements involved were extremely minute, and even if they were very much greater it would be difficult to see how weakness or rupture would be caused by them in such very ductile materials as lead or gold.

COMMUNICATIONS.

Mr. H. GARLAND (Cairo) wrote asking the authors what influence they considered the heating of the specimens, as carried out by them, would have upon the size of the crystal grains, and consequently upon the quantity of the amorphous variety present in the samples ?

Heating almost up to the melting point would, he thought, increase the size of the grains—thus diminishing the amount of the amorphous cement.

The specimens appeared to have been etched in the cold before the test, and etching usually had the effect of working out the granular boundaries in the form of fine grooves : the latter might possibly have influenced the shape of the fracture on the actual etched surface. Were any samples re-etched after fracture, and, if so, did the structure correspond to the original ?

Mr. F. C. A. H. LANTSBERRY, M.Sc. (Birmingham), wrote that Dr. Rosenhain and Mr. Ewen evidently intended to leave no stone unturned in order to develop their amorphous cement hypothesis out of the realm of pure theory. As Dr. Desch had said, "the theory is a very pretty one," and one which most metallographists would be prepared to accept when certain difficulties had been cleared out of the way. Since the theory was one which did not lend itself to direct experimental proof, it could only be settled by discussion, and it might not be out of place to refer to some of the *contra* arguments which had already been used. Professor Tammann would not consider the possibility of the existence of amorphous metal because its existence was contrary to the phase rule.

* Rosenhain and Humfrey, *Journal of the Iron and Steel Institute*, May 1913. See reply to the Discussion.

He (Professor Tammann) quite forgot that "metastability" formed sometimes a convenient loop-hole in the phase rule. It might be argued with equal force that there could be no carbide of iron in cast iron.

The phenomena of surface flow and polish would be exceedingly difficult of explanation if it were not for the conception of amorphous material. In that case, however, the layer of amorphous material could be destroyed with comparative ease. Similarly, in the case of a metal which had been strained, it was easy to conceive of the appearance of an amorphous layer along the planes of slip regardless of whether such slip were intercrystalline, or had taken place through the crystals. There, again, the material could be destroyed, and the metal restored to the state of equilibrium with the greatest ease.

There were, however, some difficulties with regard to the conception of the intercrystalline cement. In their earlier paper * the authors indicated the manner in which the hypothetical intercrystalline cement is produced. The liquid left in the intercrystalline spaces at the end of solidification was not sufficient to form "crystal units," and was therefore compelled to persist in the undercooled or amorphous condition. That was a case which differed greatly from the preceding ones, for the amorphous material could not be destroyed until the piece of metal under examination had been converted into a single crystal. The conception of the intercrystalline cement depended upon the assumption that "crystal molecules" necessarily consisted of a number of ordinary molecules, an idea which was by no means universally accepted by crystallographers. If the crystal molecules were unimolecular, then they must of necessity be absorbed by one or other of the crystals growing from adjacent nuclei, in which case they could not remain in the undercooled or amorphous condition.

In the present paper the authors gave an interesting account of the anticipated behaviour of crystalline, amorphous, and composite materials when tested mechanically (pp. 122–126). It was doubtful, however, if the line CD of Fig 1 should be drawn straight. These curves represented the behaviour of the material under slowly applied stresses, but how would such materials behave under very rapidly applied stresses?

If a piece of metal consisted of crystals surrounded and held together by a continuous network of amorphous material, then stresses must be transmitted to the crystals through the amorphous material under shock. Amorphous mat rials were known to be very brittle, so that under very suddenly applie stresses (possibly even more sudden than was applied in the Izod test) it would be expected that the fracture which would take place would be intercrystalline.

Dr. Rosenhain and Mr. Ewen wrote in further reply to the verbal discussion that Captain Belaiew would find that the process of recrystallization during annealing could be very readily explained on the amorphous cement theory. They would not, however, go into its

* *Journal of the Institute of Metals*, 1912, No. 2, vol. vii. pp. 156–7.

explanation in this place because it had already been very fully given by Dr. Rosenhain in his paper on " The Crystalline and Amorphous States in Metals " published in German in the *International Journal of Metallography,* in Berlin. A number of the other points raised in the discussion would also be found to have been dealt with at considerable length in that paper.

In reply to the communications, they (Dr. Rosenhain and Mr. Ewen) wished to inform Mr. Garland that they were quite clear that the heating to which their specimens had been exposed in their experiments could not, and in fact did not, bring about any recrystallization.

In the first place it was known that unstrained metals, even if chill-cast, could only be caused to undergo recrystallisation—if at all—by very prolonged heating, and the heating in the authors' experiments was far too brief to have affected the crystalline structure even of such materials. In the case under discussion, however, the possibility of any crystalline re-arrangement as the result of a few minutes heating was precluded by the fact that the specimens were in all cases very coarsely crystalline. This coarse crystallization had been obtained as the result of extremely gradual cooling from the molten state, and it was doubtful whether any amount of continued heating would ever produce any crystalline re-arrangement in such slowly cooled metal. As a matter of fact, however, actual examination of the structures before and after the experiments made it quite clear that no change had taken place.

Mr. Garland further appeared to think that etching in pure metals produced grooves or channels between the crystals, and that those grooves or channels might have been determining factors in locating the fractures in the authors' experiments. In reply to this it might be pointed out in the first place that in very pure metals, such as those used in the present experiments, etching did not produce grooves at the crystal boundaries, but that the dark lines seen at these boundaries under normal illumination were merely due to differences in the level between adjacent crystals. Apart from this, however, Mr. Garland's contention was disposed of by the fact that the authors broke a number of specimens in the manner described in the paper without previously etching them. The fractures were exactly the same as those obtained with previously etched specimens, and subsequent etching showed that they also followed the crystal boundaries.

With regard to the arguments advanced by Mr. Lantsberry, the questions there raised had also been dealt with very fully in the paper by Dr. Rosenhain already referred to ; they would therefore deal only with two points in Mr. Lantsberry's communication. In the first place, Mr. Lantsberry stated that the conception of the crystalline cement depended upon the assumption that " crystal molecules " necessarily consisted of a number of ordinary molecules. Mr. Lantsberry was not following the views of the authors in making this statement, and they wished to emphasize once again that the hypothesis of an intercrystalline amorphous cement was not dependent upon the crystal unit theory.

The latter had merely been advanced as a simple suggestion of one way in which the existence of an amorphous intercrystalline layer could be accounted for, and it was not fair to either of those hypotheses to regard the one as necessarily dependent upon the other. Mr. Lantsberry certainly went beyond definite knowledge, and in the authors' opinion even beyond probability, when he stated that "if the crystalline molecules were unimolecular then they must of necessity be absorbed by one or other of the crystals growing from adjacent nuclei." Knowledge of the manner in which crystals grew either in the free liquid or when the layer of liquid between two growing crystals had become very restricted, was altogether too incomplete to justify such a sweeping statement as that made by Mr. Lantsberry. In fact it was very probable that the statement in question was contrary to the truth. In a narrow film of liquid left between two adjacent crystals the fields of force arising from the two crystalline systems approaching each other would to a large extent be opposed to one another, just as the magnetic forces from two similar poles were opposed to one another, so that the field of force between two similar poles left a region in which iron filings arranged themselves haphazard. In the same way a layer of molecules between two adjacent crystals might remain in the haphazard arrangement of the liquid state simply as a result of the opposing forces of the two crystalline systems. While, therefore, the authors felt that there was considerable justification for the crystal-unit theory, they wished to make it quite clear that even if that theory were to be disproved, the hypothesis of the amorphous cement would lose nothing thereby.

Mr. Lantsberry's suggestion as to the probable behaviour of a crystalline aggregate held together by an amorphous cement when exposed to very sudden stress was interesting, but the authors were not prepared to admit that even under those circumstances fracture should be intercrystalline. It must be remembered in that connection that the intercrystalline films of amorphous matter were extremely thin, and therefore very flexible, and in those circumstances it was quite probable that under a sudden impact the amorphous layers could yield to a considerable extent by elastic bending, while the crystals themselves underwent cleavage fracture. The amorphous films would then be broken only where the cleavage of the crystals subjected them to sudden local displacements.

ON THE ANNEALING OF GOLD.*

By THOMAS KIRKE ROSE, D.Sc.

In the course of the discussion on a paper which I read before the Institute in September 1912, attention was called by Mr. F. Johnson † to the well-known effect of impurities in raising the temperature at which copper is annealed. Precise data as to the effects of known amounts of particular impurities on the annealing temperature either of copper or of any other metal appear to be lacking, and some experiments were accordingly made, which are described in Part I. of this paper. The metal chosen for the investigation was gold, for the reason that it can probably be obtained purer than other metals, and also on account of the ease and certainty with which the exact amount of impurity present can be determined.

Further observations, described in Part II., were also made on the manner in which annealing begins and proceeds.

The hardness was measured by the scleroscope, in which the "magnifier" hammer was used throughout, and also by Ludwik's cone test, using a weight of 30 kilogrammes acting for thirty seconds.

In Ludwik's machine, a cone of hard steel having an angle of 90°, as proposed by Dr. Carl Ludwik of Vienna,‡ is substituted for the ball used in Brinell's test. The hardness number is obtained as usual by dividing the load in kilogrammes by the surface of the conical impression in square millimetres. If P = the load, and d = the diameter of the impression, then the hardness number

$$H = \frac{P}{\pi \frac{d}{2} \cdot \frac{d}{\sqrt{2}}} = 0.9 \frac{P}{d_2}$$

approximately. By an arrangement of plungers working in a mercury cistern, the diameter and depth of the impression

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are measured by the height of a column of mercury in a glass tube at the time when the cone is still embedded in the test-piece. The hardness number is obtained at once from a calibration curve.

The hardness number varies with the load and with the time of action. A ball can be used instead of a cone in the machine, but Mallock * gives reasons for preferring a cone. The test-pieces must be somewhat thick (the thickness varying with the load and the degree of hardness of the test-piece), or backed up by material of the same kind, in order that trust-worthy readings may be obtained.

Apart from the saving of time, there is a further advantage in the Ludwik method of measuring the dimensions of the impression made in the test-piece. It is well known that the impression left by Brinell's ball test is not round.† Similar divergences from the circular shape occur in the impressions left by the Ludwik cone test. A photograph of two of these, made on annealed gold, is shown in Fig. 4, p. 161. The result is that it is difficult to compute the hardness number by measuring the diameter of the impression under the microscope. Probably the best results would be obtained by measuring the longest diameter, instead of taking two diameters at right angles to each other, which is the usual way. The reason for preferring the longest diameter is that the impression, besides altering in shape, contracts as a whole owing to the elasticity of the metal. Attention has already been drawn to this by M. Hanriot. ‡

These difficulties are avoided in the Ludwik method, as the diameter of the hole is measured while the cone is still pressed into the metal undergoing the test, so that the hole is still round and of the full size if the cone suffers no deformation.

Measurements made with a micrometer showed that the contraction of the impression varied in amount according to the weight applied, and also according to the nature of the metal. Thus impressions in soft annealed gold, $999 \cdot 75$ fine, suffered a contraction of $4 \cdot 4$ per cent. when the weight used

* *Proceedings of the Royal Society*, vol. lxxxvii. A. (1912), p. 470.

† For photographs, see Matweef, *Revue de Métallurgie*, vol. viii. (1911), p. 708.

‡ *Annales de Chimie et de Physique*, 8th Series, 1912, p. 421.

was 100 kilogrammes, and 9·5 per cent. when 30 kilogrammes
had been used. The impressions in lead suffered similar
contractions of 4·4 per cent. and 14·4 per cent., and the
impressions in hard-rolled cupro-nickel (copper 75, nickel
25) underwent a contraction of only 4·2 per cent. when
30 kilogrammes had been used, or less than one-third that
of lead.

PART I.

The Influence of Impurities on the Annealing of Gold.

The first experiments were made on a gold ingot of about
400 ounces troy in weight, which had been prepared in a
London refinery by electrolysis. It contained 999·75 per
1000 of gold and 0·25 of impurities, which consisted chiefly
of silver. The ingot was cast into a bar 3·15 centimetres
thick, 4·1 centimetres wide, and 51 centimetres long, and
rolled out cold to a thickness of 1·04 millimetre, or in the
ratio of about 30 to 1. The bar was passed through the
rolls sixty-three times in effecting this reduction, the heating
effect being small under these conditions.

The opportunity was taken of studying the gradual elonga-
tion of the crystals, both on the surface and at various levels
throughout the bar. It was found that besides the distortion
and lamination of the original crystals there was some slipping
of the crystals over one another both longitudinally and later-
ally, some crystals coming to the surface which were originally
in the interior of the bar.

During rolling the bar increased in width from 4·1 to 4·8
centimetres, but the individual crystals slightly decreased in
width from a maximum of 1·1 millimetre and a mean of 0·5
millimetre to a maximum of 0·9 millimetre and a mean width
of 0·45 millimetre. The width of the rolled bar was made up
by an increase in the number of crystals visible on the surface,
the bar being about 80 crystals wide before rolling, and over
100 after rolling.

The bar was about twenty-six times longer after rolling
than before, but the length of the individual crystals increased

only about twenty times, their maximum length being about 2 centimetres. It is clear, therefore, that some crystals were worked to the surface longitudinally. No evidence was observed of the division of the crystals during rolling. Photographs of the specimens were taken, but are not reproduced in this paper.

During rolling the upper and lower surfaces expanded more than the central plane parallel to those surfaces, especially in width (perpendicular to the direction of rolling), until there was a considerable overlap. Nevertheless the metal in the central plane was flattened and expanded largely, especially longitudinally, in the direction of rolling, so that the size and shape of the laminated crystals in the centre of the bar were nearly the same as those of the crystals on the surface.

The hardness of the gold continually increased during rolling, that at the centre being somewhat less than that at the surface. The initial and final hardnesses were as follows :—

	Hardness.	
	Scleroscope.	Ludwik's Cone.
Surface of bar :—		
Before rolling	4·5	22
After rolling to 1·04 millimetre . .	33·0	60
Interior of rolled bar (reduced in thickness) by aqua regia from 1·04 millimetre to 0·33 millimetre)	20·0	50

Pieces of the rolled bar gold were then annealed at various temperatures with the following results :—

TABLE I.

Temperature. Degrees Centigrade.	Time.	Hardness.	
		Scleroscope.	Ludwik's Cone.
Before annealing .	...	33·0	60
100	48 days	32·0	...
200	½ hour	30·0	...
...	21 days	5·5	...
250	½ hour	24·0	45
270	½ ,,	14·0	39
290	½ ,,	6·5	26

The hardness, as measured by the scleroscope, of specimens annealed for half an hour at various temperatures are shown in the form of a curve in Fig. 1, curve A, and the hardness as measured by Ludwik's cone test in Fig. 2, curve A.   Curve B in each figure shows the results of the annealing of pure gold prepared in 1913.   It is at once seen that the curves obtained by the two methods closely resemble one another, and this is true for all the experiments made.   The two machines appear to measure properties closely allied to one another, if not identical.

The effect of a small quantity of impurity being unexpectedly great, judging from the results given above, a number of specimens were prepared containing known quantities of silver and copper respectively.   The silver or copper was in each case added to the molten gold contained in magnesia cupels in a muffle, no covering being used.   The gold was then stirred, allowed to solidify, rolled out thin, cut up into small pieces, and again melted as before in order to obtain homogeneous alloys.   Pieces of pure gold were also melted twice in air on magnesia cupels, and other pieces were melted in a current of hydrogen on carbon capsules and on magnesia cupels.   In the latter case magnesium was reduced and absorbed by the gold.

The products were assayed with the following results :—

TABLE II.

Addition.	Gold by Assay.	Impurity by Difference.
Silver, 0·1 per 1000 . . .	999·87	0·13
,, 0·5 ,, . . .	999·35	0·65
,, 2·5 ,, . . .	997·25	2·75
Copper, 0·1 ,, . . .	999·89	0·11
,, 0·5 ,, . . .	999·45	0·55
,, 2·5 ,, . . .	997·3	2·7
Pure gold, melted in air . .	1000·00	nil
,, ,, ,, hydrogen :		
on magnesia cupel .	998·75	1·25
on carbon capsule .	999·98	0·02

It is evident that gold containing silver or copper becomes slightly less pure when melted in air, owing presumably to the absorption of oxygen.

The test-pieces after being melted were hammered into rough cubes and flattened by hammering and rolling into strips about 1 millimetre thick, when they were found to be hard. Pieces were heated in oil-baths at various temperatures for half an hour in each case, and subsequently tested for hardness, with the results given in Tables III. and IV. The results of heating some other alloys of gold are also given. For temperatures above 300°, an electric resistance heater was used instead of the oil-bath.

TABLE III.—*Scleroscope Tests.*

	Before Annealing.	Temperature.							
		130°.	150°.	175°.	200°.	225°.	250°.	280°.	300°.
Pure gold, melted in air	30	9	6	...	...	...	...	...	...
Gold, 999·9 . . . Silver, 0·1 . . .	32	11	7	...	...	...	...	...	...
Gold, 999·5 . . . Silver, 0·5 . . .	33	...	25	13	9	6	...	...	...
Gold, 997·5 . . . Silver, 2·5 . . .	34	...	28	15	13	7	...	...	...
Gold, 999·9 . . . Copper, 0·1 . . .	35	35	8	...	...	...	...	...	...
Gold, 999·5 . . . Copper, 0·5 . . .	32	...	31	31	24	16	7	...	...
Gold, 997·5 . . . Copper, 2·5 . . .	35	...	35	32	31	31	26	9·5	7

	Before Annealing.	150°.	200°.	250°.	300°.	380°.	450°.	500°.
Gold, 998·75 . . Magnesium, hydrogen, &c., 1·25 . .	35	35	35	34	35	30	7·5	...
Gold, 999·98 . . Hydrogen, &c., 0·02 .	33	25	17	9·5	7·5	...	...	...
Gold, 916·6 . . Silver, 83·3 . .	41	...	...	41	32	11	7	7
Gold, 750 . . . Silver, 250 . .	49	...	45	43	38	17	10	10
Gold, 500 . . . Silver, 500 . .	47	...	47	...	47	18·5	10	10·5
Gold, 375 . . . Silver, 625 . .	49	...	46	39	40	20	11·5	11

TABLE IV.—*Ludwik's Cone Tests.*

	Temperature.								
	Before Annealing.	150°.	175°.	200°.	225°.	250°.	300°.	380°.	460°.
Pure gold, melted in air	61	29	...	25	...	...	...	...	...
Gold, 999·5 . . . } Silver, 0·5 . . . }	61	...	39	33·5	32	...	...	...	...
Gold, 997·5 . . . } Silver, 2·5 . . . }	61	...	39	36·5	33	...	...	...	...
Gold, 995·5 . . . } Copper, 0·5 . . . }	61	60	...	56·5	39	32	...	...	...
Gold, 997·5 . . . } Copper, 2·5 . . . }	62	62	...	60·5	61	54	32	...	...
Gold, 998·75 . . . } Magnesium, hydrogen, } &c., 1·25 . . . }	61·5	...	...	60	...	61	61	56·5	30
Gold, 999·98 . . . } Hydrogen, &c., 0·02 . }	61	54	...	49·5	..	35	33	...	...

Some of the results from Tables III. and IV. are shown in the form of curves in Figs. 1, 2, and 3.
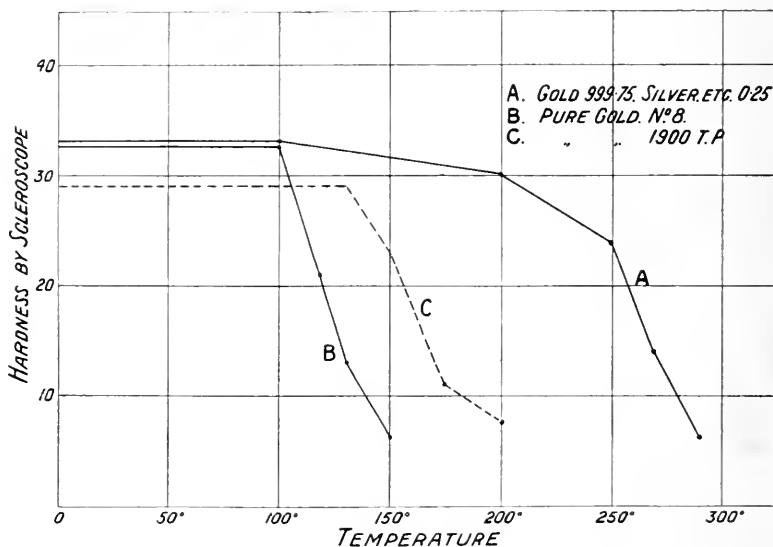
FIG. 1.
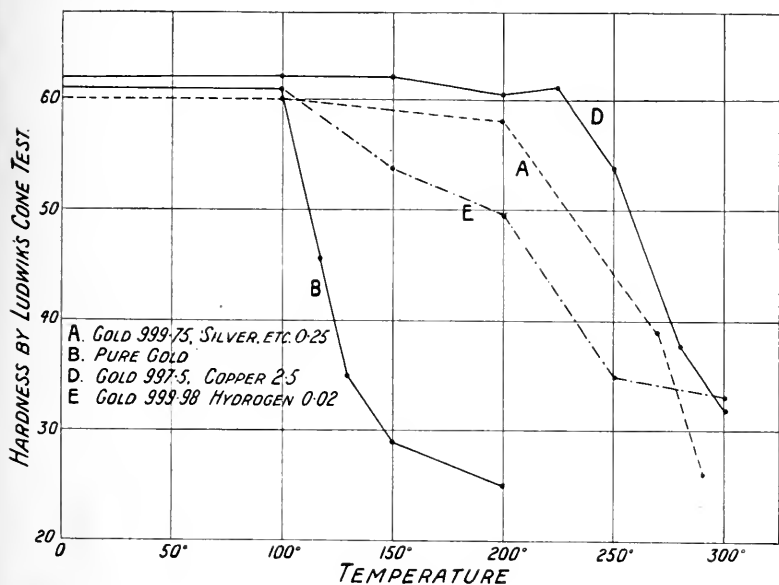
FIG. 2.
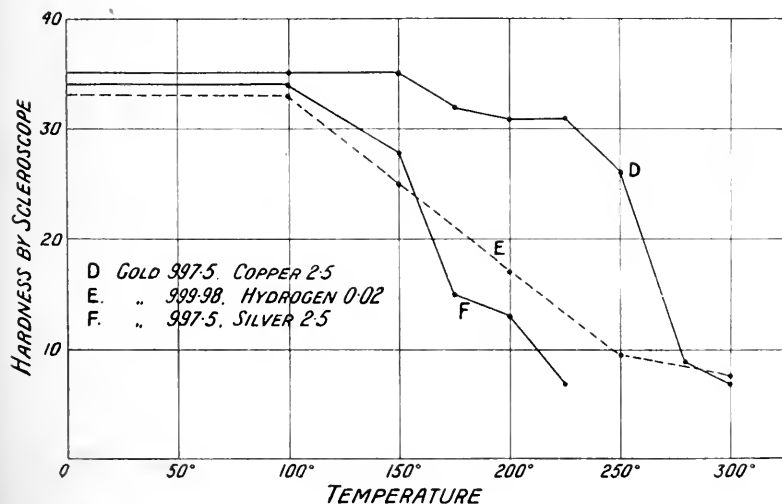
FIG. 3.

Taking the " temperature of annealing " as the temperature at which a piece of metal becomes almost completely softened and recrystallized in half an hour, the results shown in Table V. are deduced. No special importance is to be attached to this temperature. It is used here and elsewhere in the paper merely as a convenient standard for purposes of comparison.

TABLE V.

Material.	Temperature of Annealing. Degrees.
Pure Gold :—	150
Au, 999·9 ; Ag, 0·1	Above 150
Au, 999·5 ; Ag, 0·5	225
Au, 997·5 ; Ag, 2·5	Above 225
Au, 999·9 ; Cu, 0·1	Above 150
Au, 999·5 ; Cu, 0·5	250
Au, 997·5 ; Cu, 2·5	300
Au, 999·98 ; H, 0·02	Above 300
Au, 999·75; unknown impurities, chiefly silver, 0·25	290
Au, 998·75 ; Mg, H, &c., 1·25	460
Au, 916·6 ; Ag, 83·3	450

It is clear from the tables given above and from the curves that impurities in gold generally raise the temperature of annealing to an extent which can only be described as remarkably great, but that different impurities have very different effects. The effect of copper is more marked than that of silver, but other elements have far more effect than either. Gold melted on carbon in an atmosphere of hydrogen, although by assay its purity had been reduced only by two parts in 100,000, had its temperature of annealing raised from 150° to over 300°. In other cases in which the nature of the impurity was not determined, effects were observed intermediate in magnitude between those due to silver or copper and those caused by hydrogen.

Pure gold and gold-silver alloys when melted with free access of air have lower temperatures of annealing than those melted in a neutral or reducing atmosphere. Thus the ingot mentioned above (see Table I.), prepared by melting in a neutral atmosphere, although containing only 0·25 per 1000 of silver (and possibly traces of other substances), has a tem-

perature of annealing of 290°, while gold containing 2·5 per 1000 of silver, but kept melted in air for an hour, is annealed in half an hour at 225°. It may be presumed that the air removes a trace of some impurity, such as hydrogen, which raises the temperature of annealing.

The results may serve to explain the differences observed in annealing temperatures by different observers. It is probable, for example, that the annealing properties of ordinary American electrolytic copper, about 99·9 fine, are quite different from those of pure copper.

If recrystallization (and softening) is caused by the force of surface tension, as is held by Tammann, Quincke, and others, the general results were to be expected, as impurities are well known to cause a reduction in the surface tension of liquids, and presumably therefore in that of solids.

Effect of Heat on Gold Leaf.

The effect of impurities on the temperature of annealing being unexpectedly great, the question naturally arose whether pure gold leaf would contract or wrinkle under the influence of surface tension at a lower temperature than those observed by Chapman and Porter * and by Schottky,† who do not state the purity of the gold which they used. Some pure gold was accordingly beaten out into leaf 1–185,000th inch (0·14 μ) thick, but it was then found to be only 983 fine. The impurity appeared to consist of gypsum, which is used by the gold-beaters to prevent the leaf from sticking to the gold-beater's skin. With this impure gold leaf Schottky's experiments were repeated, and wrinkling observed to take place at about 320°, or nearly the same temperature as that found by Chapman and Porter for the beginning of contraction.

Annealing as a Test for the Fineness of Gold.

Experiments were also made to determine how far annealing can be used as a test for the fineness of gold, supplementary to the ordinary test by parting assay. The results are given

* *Proceedings of the Royal Society*, vol. lxxxiii. A. (1910), p. 65.

† *Nachrichte der Kaiserliches Gesellschaft der Wissenschaften zu Göttingen*, 1912.

in Table VI., the time of annealing being half an hour in each case.   The hardness is given as measured by the scleroscope.

TABLE VI.—*Fine Gold.*

Temperature. Degrees.			No. 6, Au 1000·00.	No. 7, Au 999·94.	No. 8, Au 1000·00.	Trial Plate of 1900, Au 999·96.*	Trial Plate of 1873, Au 999·98.
Before Annealing			35·0	33·0	33·0	35·0	27
100	.	.	35·0	...	33·0	...	...
118	.	.	27·0	...	21·0	...	...
130	.	.	18·0	29·0	13·0	35·0	...
150	.	.	6·2	30·0	6·4	23·0	12
175	.	.	...	10·0	...	11·0	...
200	.	.	5·4	8·5	...	7·5	7

These samples of gold were all prepared by precipitation of gold from specially purified gold chloride by means of sulphurous acid, followed by washing and melting.   The " temperatures of annealing " are as follows:—

<div style="text-align:right">Degrees.</div>

No. 6   .   .   . 1000·00 fine   150
No. 8   .   .   .   ,,   ,, ...   150
1873 T. P.   .   . 999·98 ,,   .   .   . above 200
1900 T. P.   .   . 999·96 ,,   .   .   .   ,,   200
No. 7   .   .   . 999·94 ,,   .   .   .   ,,   200

The specimen of gold with the lowest " temperature of annealing " yet observed was obtained by melting fine gold No. 8 in a magnesia cupel in a muffle with free access of air.   Its annealing temperature was about 130°, at which temperature its hardness was reduced in half an hour to 7 as measured by the scleroscope or 32·4 by Ludwik's cone.

In this connection it may be mentioned that fine gold is made finer by heating it to redness, as was first observed by my colleague, Mr. S. W. Smith.   The change is presumably due to the removal of grease, condensed vapours, &c., from the surface.

It is clear from these results that, given a particular method of preparation of pure gold, its purity can be easily and quickly tested by annealing it.   By the parting assay, the composition of fine gold can be determined correct to

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* This gold becomes 1000·00 fine when heated to redness in air.

0·01 per 1000 by taking the mean of about twenty assays of
each sample, weighed to 0·01 per 1000, the amount of metal
required for assay being about 10 grammes in each case.
If, however, pieces weighing about a gramme of each of the
samples in Table VI. are heated at 150° for half an hour,
they can be readily distinguished from one another, either by
the scleroscope or by Ludwik's cone, or by etching them in
aqua regia. (The best medium for etching is aqua regia
diluted with an equal volume of water, acting at the ordi-

Fig. 4.—Impressions made by Ludwik's Cone in Annealed Gold.
Magnified 15 diameters and slightly reduced.

nary temperature for about an hour. Pure gold becomes
recrystallized at 150°, but impure gold merely shows the
original laminæ.) The method is now in use at the Royal
Mint to determine whether any new sample of " proof " gold
is pure or not. Impurities amounting to one or two parts in
100,000 are readily detected, and probably with greater care
far smaller quantities of impurities would be observable, if
any means existed of checking the results by the direct
determination of such small amounts. Possibly something
may be done in this direction by the spectroscope.

PART II.

RECRYSTALLIZATION ON ANNEALING.

A study of the partly annealed specimens of gold referred
to in Part I. showed that recrystallization and softening does
not take place simultaneously throughout the mass, but
occurs in particular laminæ or flattened crystals, while others
remain unchanged until more time has elapsed or the
temperature has been raised.   In Fig. 5 a photograph is
reproduced showing recrystallization in gold 999·75 fine, after

FIG. 5.—Gold, Specimen A.   Annealed at 250°.
Magnified 4 diameters and slightly reduced.

it had been heated at 250° for half an hour (specimen A,
see below).   The metal was heated in an oil-bath, continually
stirred, immersed in another oil-bath, which was also stirred.
The temperature was constant throughout the bath, so that
all parts of the sheet of metal were equally heated.   One of
the laminæ in this specimen is seen to consist of a string of
new crystals, while the laminæ on each side of it are un-
affected.   The other face of the specimen is shown in
Fig. 6.

Figs. 7 and 8 show opposite faces of another plate of the
same gold (specimen B) heated to 270° for half an hour.
The less altered laminæ are here speckled with very minute
new crystals.

Fig. 9 shows a plate of the same gold (specimen C) heated to 290° for half an hour. In this case all the laminæ have undergone recrystallization except one in the centre of the

FIG. 6.—Gold, Specimen A. Annealed at 250°.
Magnified 4 diameters and slightly reduced.

field, which shows no change even under higher powers of magnification.

The new crystals do not at first increase in size, or as a general rule pass the original boundaries of the old distorted
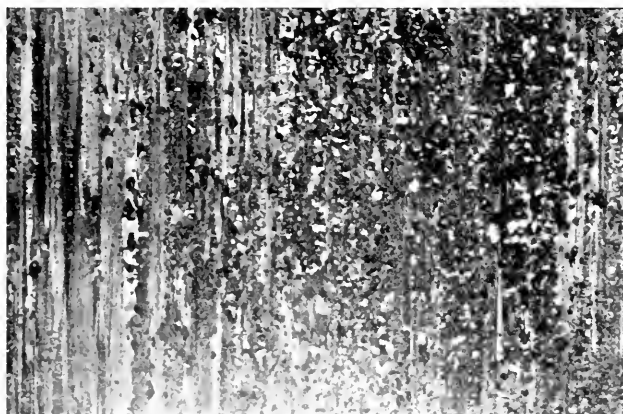
FIG. 7.—Gold, Specimen B. Annealed at 270°.
Magnified 4 diameters and slightly reduced.

crystals, but if heating is continued, they soon begin to eat into the original boundaries, which are gradually obliterated. The crystals subsequently increase in size and diminish in number, as is well known.

FIG. 8.—Gold, Specimen B. Annealed at 270°.
Magnified 3½ diameters and slightly reduced.

FIG. 9.—Gold, Specimen C. Annealed at 290°.
Magnified 15 diameters and slightly reduced.

The new crystals appear to be quite soft, and the un-
altered laminæ as hard as before the annealing began. The
measurement of the hardness of a single thin layer presents
some difficulty, as large numbers of them are piled on one
another, of which some may be hard and some soft. The
number of crystals counted on two lines drawn across the
edge of the bar before rolling, vertically to the face, were
fifty-three and fifty-five. Assuming that the rolled plate is
fifty crystals thick, the thickness of each lamina would be
only about 0·02 millimetre, and Ludwik's cone would mea-
sure the mean hardness of at least thirty or forty of them,
whilst the scleroscope would measure the mean hardness of
about twenty of them. It is, therefore, perhaps surprising
that the recrystallized parts should show a much lower hard-
ness than the uncrystallized parts when tested by these
machines. Yet such is the case.

In one little plate from the ingot, already referred to,
measuring 1·05 centimetre × 0·8 centimetre and 1·04 milli-
metre thick, recrystallization had occurred towards one side
of the specimen and not at the other. The hardness was as
follows :—

	By Scleroscope.		By Ludwik's Cone.	
	Mean.	Limits of Readings.	Mean.	Limits of Readings.
Before annealing	33·0	...	60	...
After annealing at 250° for half an hour .	...	...	...	...
Part unaltered on surface . . .	27·6	25 to 31	51	48 to 53·4
Part recrystallized on surface . .	17·3	13 to 21	40	37·6 to 42

The wide range of the determinations of the hardness of
the partly annealed specimen (13 to 31 by the scleroscope,
and 37·6 to 53·4 by the cone) shows that the mean hardness
as given in Tables I., III., and IV. expresses the facts very im-
perfectly.

In specimen A, Figs. 5 and 6, B, Figs. 7 and 8, and C

Fig. 9, which were pieces about 5 centimetres square, the hardness was at follows, by Ludwik's cone :—

	Part Unaltered on Surface.	Part Recrystallized on Surface.
Before annealing	60·0	...
A, annealed at 250°	58·0	46·0
B, annealed at 270°	43·2	35·4
C, annealed at 290°	27·2	25·1

It appears, then, that the surface indication of softening corresponds to a real comparative softening in depth, and that recrystallization spreads in depth from one lamina to another more readily than sideways, so that superposed laminæ are more likely to be similar in hardness than those placed side by side. It follows that partly annealed metal consists of alternate strips of hard and soft material, and consequently that such metal has weak places where its rigidity and resistance to rupture are little higher than those of fully annealed material.

DISCUSSION.

Mr. H. L. SYMONDS (London), in opening the discussion, said that he was afraid that the ordinary manufacturer among the professors was a sort of minnow among the pike. The paper was particularly interesting to him in his own trade as a goldsmith and silversmith. One of the previous speakers had said that one of the great objects of the Institute was to help forward the various industries, as they had been doing in Corrosion research work, by means of technical knowledge possessed by so many members of the Institute. He would be very glad indeed if that idea could be brought into play in connection with the working of gold and silver; but he was somewhat disappointed in looking through Dr. Rose's paper to find that he was dealing, by way of illustration, with practically pure gold only. That was the metal which probably came under Dr. Rose's own ken; but he would remind them that in the commercial world they dealt with tripartite alloys of gold, silver, and copper, and with regard to the greater part of the gold (9 carat) used in commerce, it was really copper alloyed with gold. Dr. Rose had given an illustration of a working alloy composed of 750 parts of gold and 250 parts of silver. That was practically an unknown alloy in commerce. The alloy they knew most of consisted of copper, approximately 465 parts, gold 375 parts, and silver or zinc the rest. He thought the most practical point in the whole of Dr. Rose's paper was that in which he laid stress upon the importance of the condition of the constituents, and also of the advantages that sometimes could be obtained by doubly melting the material. That was entirely in accord with his own firm's experience. They had very often found, in practice, that when gold would not work at the first time, by some miracle it would work remarkably well when melted up again.

Dr. ROSENHAIN, F.R.S., Member of Council, said that he greatly appreciated Dr. Rose's paper, which was a remarkable study of a subject which had not received as much attention as it deserved. Some considerable time ago he had been associated with Sir Alfred (then Professor) Ewing, studying the annealing of lead; they were not fortunate enough to have at their disposal adequate quantities of gold, and so they had to content themselves with the baser metal. The results that Dr. Rose had shown in his paper were of extraordinary interest. They showed that the mechanism of annealing was not strictly identical in various metals. The mechanism of annealing in gold was distinctly different from that in lead, and the growth of the crystals did not appear to take place by branching out, to anything like the same extent as in other metals. Then he referred to the suggestion that recrystallization was due to surface tension. With that he entirely disagreed. If it were true that annealing altered the shape of the elongated crystals and drew them together again into something like spherical grains, so as to diminish the total area of the boundaries, then the action might be ascribed to surface tension; but he would point out that they had a single crystal

breaking up into a large number of small ones, and so for the surface-tension theory the energy contained in the boundaries was greater in the freshly annealed metal having a large number of small crystals than it was in the strained metal. It was impossible to suggest that such a change was due to surface tension.

Professor T. TURNER, M.Sc., Vice-President and Honorary Treasurer, said that he had read this paper with very much interest, and had taken notice of the hardness tests, which Dr. Rose had adopted, and they appeared to compare with those mentioned on a previous occasion. One matter which struck him particularly, in those curves and diagrams, was the abruptness of the change of properties as between hardened and soft material under annealing. That had, of course, already been to some extent indicated by Beilby, and they had some examples of that effect in the photomicrographs which Dr. Rose had shown. When they heated a metal below a certain temperature, there was very little change. Then they came to a sudden and sharp change of direction in the curve, and beyond that for some distance again there was very little change. When they came to look at the photomicrographs, they saw that part of the material was amorphous and part definitely crystalline. That meant that there was no gradual change from the amorphous to the crystalline. It was either amorphous or crystalline. In connection with the hardness tests also, the metals were either definitely hard or definitely soft ; there was an abrupt transition point. That varied according to the purity of the metal. Dr. Rose was merely extending the work of Roberts-Austen, whose name was associated with the researches conducted at the Royal Mint, in pointing out the extreme importance of the first trace of impurity in affecting the properties of alloys.

Dr. ROSE, replying on the discussion, said that he did not know that there was very much to say beyond acknowledging the kind remarks made. In that particular case no choice was left to him as to what metals or what alloys should be dealt with. It was obvious that in finding out what was the action of impurities, they must first of all use pure metal, as from this point of view any alloying metal would act as an impurity. The action of impurities on the annealing properties of alloys was very slight. When one was dealing with nine-carat gold, small impurities would not make very much difference to the working properties, except that they might make the metal brittle. The alloy of 750 gold and 250 silver was used for trial plates. The alloy of 750 gold and about 125 of silver and 125 of copper was used for wares, and it would be easy to try the effects of impurities on that alloy, if there was anything to be gained by it.

That matter about surface tension, which Dr. Rosenhain mentioned, could not be so easily disposed of as Dr. Rosenhain seemed to think. All the metals in the hard state possessed large numbers of slip planes, and the surface tension was assumed to act at the slip planes in exactly the same way as at the surface of the crystals. When annealing took place,

those slip planes altogether disappeared, and the surface tension with them. The sum of the surface tension would thus diminish although the number of crystals increased. This had been stated by Tammann.

With regard to Professor Turner's remarks, he would say that all his results tended to show that although there was a rapid change on annealing, there was not one critical point, but a small critical range of temperature in each piece of metal.

COMMUNICATIONS.

Dr. T. K. Rose (London) wrote in further reply to the discussion that he had not perhaps made it clear to Mr. Symonds that the improvement in the working quality of gold due to a second melting was due to the oxidation of impurities, such as lead, which made gold brittle. The same result could be attained in the first melting, either by omitting the usual charcoal cover or by adding a little oxide of copper, say 0·1 per cent.

He could not agree with Dr. Rosenhain that there was as yet any evidence that the mechanism of annealing differed in different metals. The growth of crystals, by branching out, observed in lead at 200°, was similar to the growth of crystals in gold at a somewhat higher temperature. The formation of crystals in pure gold at 150° was similar to that which appeared to take place in lead at about 0°, but the latter had not yet been fully studied, and was not dealt with in the memoirs of Ewing and Rosenhain.

Mr. F. Johnson, M.Sc. (Birmingham), wrote to express his great appreciation of the admirable paper presented by Dr. Rose. He (Mr. Johnson) contemplated undertaking a similar work in connection with copper, and, in fact, had already made some exploratory experiments, so that, for him, Dr. Rose's paper had come at a very opportune time. He wished to make one comment, and that was in reference to the extraordinary influence of 0·02 per cent. of hydrogen in raising the temperature of annealing of gold from 150° to over 300° (see Table V.). He trusted that, in view of the importance of the presence of gases such as hydrogen in other commercial metals and alloys, that remarkable influence would be confirmed by Dr. Rose.

Dr. W. Rosenhain, F.R.S., Member of Council, wrote that Dr. Rose, in his verbal reply to the discussion on his paper, asked him (Dr. Rosenhain) to deal at greater length with his objections to the theory that surface tension played a large part in the process of re-crystallization by causing the elongated crystals to be replaced by equi-axed ones. Since that discussion took place, some fresh evidence had been published which showed clearly that the mere fact of possessing an elongated shape did not of itself render a crystal unstable. Stead and Carpenter, in their paper on the crystallizing properties of electrolytic

iron,[1] showed several examples of iron containing extremely elongated crystals which possessed no marked tendency to revert to an equi-axed shape on annealing at temperatures where the annealing of *strained* iron with far less markedly elongated crystals took place rapidly. If the recrystallization were merely the result of surface tension tending to reduce the area of bounding surfaces, the rate of readjustment would depend only on the shape of the crystals, however they might have been produced. The suggestion implied in the whole of the surface tension theory was that that tension could and did overcome the "crystalline forces" to the extent of bringing about material rearrangement of the crystals. But there was much evidence to show that such could not be the case. If surface tension were so powerful a factor at the bounding surfaces of crystals, the multiform dendritic crystallization which was so frequently seen could not occur except under special conditions where the crystallization took place so fast that the "surface tension" forces might not have time to produce their effects. But those dendrites might be formed quite slowly. Indeed, the study of incipient crystallization in salt solutions showed clearly that while the "crystallites" were very minute (almost ultra-microscopic), their form was largely governed by surface tension, yet so soon as they attained appreciable size the rounded forms tending towards spherical drops or rounded films gave place to the sharp angles and often elongated shapes determined by crystalline forces and opposed to "surface tension." That led him (Dr. Rosenhain) to the view that, as compared with the forces at work in bringing about crystallization, surface tension forces at crystal boundaries were negligibly small.

That argument was so far principally directed against the "surface tension" explanation of recrystallization as put forward by Tammann, on the view that there could not be any amorphous metal at all. Dr. Rose took a slightly different view by suggesting that in the strained metal there existed a large number of crystalline lamellæ surrounded by amorphous metal ; if he (Dr. Rosenhain) understood him rightly, Dr. Rose then suggested that, under the action of surface tension each of these lamellæ would contract into a minute equi-axed crystal, and that each of those would then grow at the expense of the surrounding amorphous metal. There was, however, a fundamental objection to that view so far as any intervention of surface tension was concerned. Deformation by slip did not really result in the formation of lamellæ at all—when a crystal was forced to change its shape, slip must of necessity occur simultaneously in *several* directions—generally at least three—and on each of those sets of slip surfaces, *if the deformation had been severe*, a layer of amorphous metal was formed ; but the resulting structure would not be that of lamellæ embedded in amorphous metal, but of small nearly or quite equi-axed crystal bricks or elements surrounded on all sides by amorphous layers. Moreover, all those elements would usually remain co-oriented throughout the original crystal, and if they grew on annealing one would expect them to reconstitute the old

crystals. That that did not occur was probably due to disturbances which arose near the crystal boundaries, where a certain number of crystal bricks on either side of the original boundary were probably twisted out of their original orientation owing to the " friction " of the adjoining crystal. It seemed probable that recrystallization would begin at those points where the *local* disturbance had been greatest, and thus that some of those disoriented crystal " bricks " would become the centres or neuclei of new, small equi-axed crystals. It might be asked why those " disoriented " bricks should cause more active growth than their fellows, which had only been displaced without twisting? To that it might be replied that even if the relatively undisturbed bricks or elements began to "grow" by inducing the surrounding amorphous layers to return to crystalline orientation, the effect on the appearance of etched surfaces would be very slight—since it would merely cause the more or less complete reversion to the crystalline state of the elongated large crystals, and those on etching would *look* no more crystalline than they did in the freshly-strained state. But there was another reason ; the power possessed by a crystal or crystal element to induce crystallization in amorphous metal surrounding it was not the same for all directions in the crystal—the influence on surrounding molecules was almost certainly greatest near the crystallographic planes of densest packing. Now if a number of crystal elements were thickly scattered in an amorphous matrix, each pair would compete for the possession of the amorphous film lying between them and—if they were all similarly oriented, as in the body of a strained crystal—they would exert influences almost or exactly equal. If the orientation had been disturbed, however, cases would occur where a very "strong" or aggressive face on one element or brick was opposed by a very " weak " face on its nearest competitor. It followed that here and there some favoured individual " bricks " would grow rapidly and give rise to the small equi-axed crystals seen in some of Dr. Rose's photographs.

He (Dr. Rosenhain) had gone somewhat fully into that question, in order to show how clearly and simply the whole of the phenomena could be explained on the basis of the " amorphous " theory, without the intervention of " surface tension." Only one further point need be mentioned. The thermo-dynamics of the annealing process were sometimes explained on the basis, that the surface tensions on the elongated crystals represented a larger quantity of potential energy than the same tensions on the equi-axed crystals resulting from annealing. That argument applied with much greater force to the condition of numerous minute crystal bricks surrounded by amorphous films, such as had been discussed above, although it must be borne in mind that the amorphous material was only *slightly* less dense than the crystalline, so that the surface tensions must be extremely small and the potential energy correspondingly minute. On the other hand, the energy side of the question was much better met by the amorphous theory (without the intervention of an amorphous phase, the surface tension theory became quite untenable, as he pointed out in the verbal discussion). The amorphous

material contained a large amount of latent heat—corresponding to the heat which was liberated when a molten metal crystallized. That heat had been stored in the amorphous metal, being absorbed as part of the work done in straining the metal. The "stored" energy tended to "run down" in accordance with the second law of thermo-dynamics, and thus provided an ample supply of energy to set recrystallization in motion. There was thus a known, definite, and large accumulation of energy to account for the phenomena, without having recourse to the very dubious "surface tension" idea.

Dr. Rose wrote that in reply to Mr. Johnson's suggestion he would certainly try the effect of hydrogen on gold again, although he had no reason to doubt the results of his previous experiments. He would point out that he had no conclusive evidence that the impurity of 0·02 per 1000 (not 0·02 per cent. as stated by Mr. Johnston) in the gold consisted of hydrogen. He would examine that point also. The definite conclusion arrived at was that melting gold in air did not diminish its purity, and actually lowered its temperature of annealing, but that melting it in hydrogen very slightly diminished its purity and greatly raised its temperature of annealing. The results would almost certainly be different with copper, and he was glad to hear that Mr. Johnson was about to investigate the matter.

In reply to Dr. Rosenhain : he objected to the suggestion that an elongated shape ought of itself to render a crystal unstable. An elongated shape might go with comparative massiveness if the magnitude of a crystal were not exceedingly small in any direction. Crystals elongated by rolling or crystals flattened and expanded (either by hammering or cross-rolling), without their equi-axial shape in two directions being disturbed, were alike subject to recrystallization on being annealed. But this was because they were exceedingly thin. There was little if any evidence of *unstrained* metals undergoing recrystallization on annealing. He was trying to supplement the evidence on that point and so to confirm or disagree with Dr. Rosenhain's own observations made in 1900. The reason was probably that unstrained crystals were never very thin, or rather, one should say, they were never much smaller when measured in any one direction than in any other. There was certainly some difference in physical conditions between electro-deposited metals and metals cast as far as possible without straining effects. If these facts conflicted with the surface-tension theory so much the worse for the theory. But they did not. They agreed perfectly with the surface-tension theory, and showed how little force there was in Dr. Rosenhain's first contention.

Then, with regard to dendritic crystals, he would point out that dendritic crystals were not single crystals but groups of crystals, and that each element was a sort of crystal brick not far removed from the equi-axed condition. The whole theory of the influence of surface-tension was based on the supposed relative superiority of " crystalline forces " to the forces of "surface-tension" at low temperatures, and their relative

inferiority at higher temperatures.   Hence it was beside the mark to cite the formation of sharp edges and elongated shapes in crystallization at ordinary temperatures.   Sharp edges and elongated shapes were seldom formed in metals crystallizing from a molten state.   That difference alone constituted a strong argument in favour of the " surface-tension " theory. Besides there were the curved faces of diamonds and other crystals to be borne in mind.   To submit that " surface-tension forces at crystal boun-daries were negligibly small " was to fly in the face of all the evidence.

Dr. Rosenhain next proceeded in his second paragraph to argue in a highly ingenious manner on behalf of the " amorphous " theory, and began by attributing to him (Dr. Rose) a view as to the exis-tence of amorphous metal, which had never entered his head.   In the whole paper on the " Annealing of Gold " the word " amorphous " was not even mentioned.   Theory was well-nigh excluded.   He (Dr. Rose) was deficient in the love of theory which just now was absorbing so much energy.   He preferred to experiment, and to theorise as little as possible. A theory, however, was welcome to him in proportion to its simplicity, and for that reason he was not attracted by the " amorphous " theory, which led to much abstruse and complicated reasoning, and had given him no real help.   Certainly he had not suggested that crystals grew at the expense of surrounding amorphous material, in the existence of which he had not brought himself to believe.   He believed that they grew at the expense of other crystals which were in a state of strain, or at any rate in a metastable condition from that or some other cause. The formation of slip planes might relieve without altogether removing the strain.   The strain would involve the existence of a force tending to restore the previous state and so to assist the force of " surface-tension " in forming equi-axed crystals.   The parts under greatest strain would be the first to recrystallize.   Highly strained metal had been found by Tammann to have a lower annealing temperature than slightly strained metal, and he (Dr. Rose) was about to confirm the results by working on very pure metal.

Generally speaking, the middle of an elongated flattened crystal would be more highly strained than its edges, and new crystals on the whole were formed more readily in the middle of the strips than at their edges. There was evidence, too, which should be tested by further observations that the new crystals extended through several superposed lamellæ, forming equi-axed crystals in all three directions.   How to fit all that in with the amorphous theory appeared to pass the wit of man, but there were no difficulties if the " surface-tension " theory was adopted.

Dr. Rosenhain suggested that the cause of recrystallization lay in the existence of some " disoriented " bricks which could not be seen or their presence detected in any way.   He gave no reason why crystal-lization should begin around these bricks.   He did not say why one face of a crystal element or brick should be a " strong " or aggressive face and another a " weak " face.   He could think of no reason why recrystallization should occur at all except that it did.   [" The power possessed by a crystal or crystal element to induce recrystallization in

amorphous metal surrounding it."] There was no hint that he had pictured to himself the nature of the force existing in the crystal element which was adequate to produce recrystallization. In fact, if the forces of surface tension and strained metal were given up there was nothing to take their place. Dr. Rosenhain did not even suggest that amorphous metal was in a metastable state and liable to revert to the crystalline state spontaneously. If he had, the answer would have been that in that case recrystallization should begin between the distorted crystals, not inside them.

Dr. Rosenhain had not taken into account the fact that impurities raised the temperature of recrystallization. This was explained by the " surface tension " theory, but how could it be true if one accepted the amorphous theory? He would like to think that he had resolved all Dr. Rosenhain's doubts, and that henceforth he would be a supporter of the " surface tension " theory.

THE SPECIFIC VOLUME AND CONSTI-
TUTION OF ALLOYS.*

By W. M. GUERTLER, Doc.Met., Ph.D.

In a former paper, read before the Institute of Metals in the autumn of 1911, I discussed the legitimate connections between the electric conductivity of alloys and their constitution, with special reference to the manner in which these relations could be used for investigating the constitution with the aid of specific resistance determinations. It was possible in this manner to establish a so-called " resistometrical " method which can render valuable aid as a complement of other systematic research methods.

I duly compared this method with the thermal method which was previously mostly employed, and pointed out the difficulties, from the point of view of principle, which must always be encountered with the thermal method ; and I gave emphasis to the contrast existing between those methods in which the temperature at any moment can be maintained constant for any length of time, and the establishment of equilibrium ascertained, and the thermal method which is always associated with the fact that temperature variations take place fairly slowly. I further pointed out that the thermal method must therefore always fail where the equilibria cannot establish themselves at all without the temperature being maintained constant for a fairly long time.

I stated at that time that the same advantages which the resistometrical method possessed over the thermal method could also be attributed to the dilatometrical method, which consists in following the specific volume or the specific gravity. An alloy can be slowly heated and cooled and its volume continuously followed in this manner ; and when in this connection irregularities show themselves, or when the values obtained on cooling and heating do not coincide perfectly, any desired temperature may be maintained constant for any length of time until the state of equilibrium in the

* Read at Annual Autumn Meeting, Ghent, August 29, 1913.

alloy is attained, such state being recognized by the fact that
the specific volume does not further undergo alteration at
this constant temperature.

As in the case of the resistometrical method, the first
question was as to whether the specific resistance or the re-
ciprocal of the same (the specific electric conductivity) should
form the basis of the measurements and calculations, so
the question confronting us in the dilatometrical method is
whether the specific gravity or its reciprocal (the specific
volume) should be taken as a basis.   The answer to this is
very simple ; indeed it is very difficult to understand how in
earlier times down to within the last few years the specific
gravity should have been taken as the basis.   Maey first
pointed out in 1901 that, in a heterogeneous mixture of
two substances, only the specific volume, and not the specific
gravity, can be a linear function of the mixture.   By observ-
ing the specific volume we are enabled, by proceeding from
the straight connecting line of the volumes of two components,
to recognize all irregularities which are manifested by a devia-
tion from the straight line and which point to the occurrence
of new phases in the mixture.

In homogeneous solid solutions we are, of course, unable *a
priori* to presume such a linear condition as a function of the
concentration, though experience shows that the deviations
from the straight line are certainly not considerable.

Finally, as regards the dependence of the volume on the
temperature, we know that this very closely approaches the
linear condition for most metals over moderate ranges of
temperature.

All of the above reasons considerably simplify the diagrams
which will be constructed later to demonstrate the dependence
of the volume on concentration and temperature.

The base lines derived apply, strictly speaking, only in the
case of alloys built up of metallic crystals in such manner
as to completely fill up the space.   It is, of course, perfectly
evident that porosity and hollow spaces impair the values ;
but we have also to reckon with irregularities which must
occur to a certain extent even in a perfectly dense alloy.   In
an isolated crystal the molecules have a certain mutual

position, which is regular and unvaried, and which opposes a great resistance both to compression and dilatation. The specific volume of a single crystal is therefore perfectly unequivocally defined, the molecules being most densely packed. The conditions are different in an aggregate of different crystals. When the individual crystals also possess the characteristic and most dense packing, the packing in the space between every two crystals may not, however, be just as dense, since the two neighbouring crystals (oriented in different directions) cannot accommodate themselves exactly. We must assume (in concordance with the interesting theory of the " amorphous " intermediate substance, which has been propounded by Beilby and further developed by Rosenhain) that the intermediate spaces between the individual crystals are characterized by spaces in which the densest packing does not exist—that is to say, where we have empty intermediate spaces of molecular dimensions. The more fine-grained the aggregate, the greater number must we have of such intermediate spaces, and the greater, therefore, must be the specific volume of the aggregate. These variations are, of course, very slight. By studying the relative amount of these changes in volume in comparison with the specific volume itself, we may even obtain information concerning the ratio of the molecular magnitude to the crystal magnitude.

It is a well-known fact in the case of alloys of two metals not forming solid solutions with each other to a measurable extent, and which undergo a mutual lowering of their melting point, so that a eutectic point is formed, that the eutectic in question possesses a much finer grain than the excess primary crystals of one or other of the components. The greater the amount of space given over to the eutectic in the alloy, the more perceptible are the influences of this fineness of grain ; and we thus come to the conclusion that the specific volumes of the pure eutectics must be slightly greater than would be calculated from the values of the pure components by the mixing rule. The same applies to eutectoids, and also to pearlite ; and the phenomenon, of course, is all the more pronounced the finer the eutectoid—that is, it is more pronounced in sorbite than in pearlite, and again, more evident

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in troostite than in sorbite. Where the fineness of the heterogeneous constituents of troostite are nearly molecular, we must have in this case a maximum of this increase in volume, owing to increase in the fineness of grain.

It is at once evident, however, that the order of magnitude of this variation is very small, so that these phenomena only make their influence felt in extremely careful experiments.

What we have just said also explains the influence of mechanical treatment on the volume, the effect generally being twofold where a normal alloy is hammered, rolled, or the like; for (1) small hollow spaces, pores, &c., contained up to a certain degree in every piece of metal close up—this process ceasing when all these hollows have closed up; (2) as the individual crystal grains of the aggregate are broken up, the grain becomes finer. This process goes on continually so long as the treatment continues—that is, it never comes to a standstill.

The co-operation of these two factors will thus cause the specific volume first of all to decrease (since the first factor outweighs the second) then to attain a minimum, and again increase so soon as the first factor is removed by the closing up of all the cavities. We thus come to an explanation of the very important, and, at the first glance, very surprising observation first made by Wertheim in 1848, this observer having undoubtedly established the fact that the volume of metals and alloys can be increased by intense mechanical treatment.

With reference now to the methods, we must at the outset distinguish between two ways which differ in principle. On the one hand an investigation can be made upon bars whose changes in length are measured; in this case only one dimension of the dilatation is studied. Or, samples of the alloy are immersed in a liquid contained in a flask having a long thin neck, and the displacements in the level of the liquid in this thin neck are observed as a function of the temperature. Thus when the changes in the volume of the vessel and the liquid are known, the changes in volume of the alloy can be calculated. If, however, the dilatation of the flask and the liquid is not known, we must abandon

the idea of determining the absolute values of the dilatation of the metal under investigation; but we may plainly follow discontinuities which may eventually occur, by representing the position of the mark in the neck graphically as a function of the temperature, and thus determine the temperature points where new phases in the system occur or disappear, obtaining thereby a means of investigating the constitution. This method is distinguished from the former by the fact that the changes in volume are measured cubically, the intensity of these changes in volume thus being the third power of the variations measured by the linear method. Another method of determining the cubical expansion consists in the direct determination of the specific gravity with the aid of an immersed sinker.

It may, however, be objected that the expansion of the crystals is different in the different directions, and that therefore the linear expansion of a bar must depend upon whether the individual crystals of the same predominate in a direction parallel to the longitudinal direction of the bar or perpendicular to it, or are oriented irregularly. The expansion in volume by the cubical method is quite independent of these factors. Thus while we must observe certain irregularities when using the first method when investigating a wire or a bar, (1) in a hard-rolled or a hard-drawn condition, and (2) in an annealed state, the cubical method will not show these irregularities, since annealing has the effect of doing away with the longitudinal extension of the crystals.

In order to give briefly as comprehensive an idea as possible concerning the changes in volume which may be expected in the individual alloys of different types of constitution as a function of the temperature and concentration, the following figures will now be described.

Fig. 1 demonstrates the simple case in which the two components are intermiscible in all proportions, both in the liquid and the solid state. Proceeding from the first pure metal A, we find, first, its volume to vary as a function of the temperature on a nearly straight line reaching continuously from the ordinary temperature to the melting point. At the melting point, expansion generally takes place (bismuth is excepted). The change must under all circumstances be brusque, the

volume suddenly assuming a different level and moving, with further rise of temperature, on a new curve corresponding to the liquid state.

If now we consider an alloy containing, say, 10 per cent. of the second metal B, we find this to show over the range of the crystallized state an expansion curve running more or less parallel to the expansion curve of the pure metal A, until the solidus curve is reached ; and the dilatation curve connected with the transition into the liquid state now makes itself perceptible. Only when the temperature of the liquidus curve is exceeded is melting completed, and the further expansion is completed on a new curve which again corresponds to the perfectly liquid state and which will run approximately parallel to the dilatation curve of the liquid (pure) metal A.

If, now, in the same manner, we follow further additions of B, we again get analogous branches of the curve for the solid state up to the solidus, for the semi-liquid state between liquidus and solidus, and for the fluid state beyond the liquidus. In the case of the pure metal B, liquidus and solidus again coincide, and the value for the volume assumes a vertical position on the attainment of the melting point.

We thus get an area $a\ b\ d\ c$ for the solid state, an area $e\ f\ h\ g$ for the liquid, and in between an area $c\ d\ f\ e$ for the semi-liquid state. The shape of these areas is shown in Fig. 1 by adding a series of curves corresponding either to constant temperature or constant composition. In the area of the perfectly crystallized or perfectly liquid state the shape is fairly simple, being, however, somewhat more complicated in the area of transition between the two.

Fig. 1A represents the condition diagram of the system shown in Fig. 1 without taking into account the volume in a temperature-concentration diagram. Let us, for example, consider a single concentration at the temperatures m, n, o, p, q. At m everything is liquid, and at q everything is crystallized ; the volumes of these two extreme points are thus easily determined by the volume-areas of the solid and liquid states. The point o lies midway between the two as measured in vertical intervals ; it is, however, not equidistant from liquidus and solidus as measured in horizontal intervals, but is about

twice as far from the solidus as from the liquidus. From a known law we thus find that the relative quantities of liquid and crystals in equilibrium with each other at this temperature are as $2 : 1$. The volume of the mixture selected, at a temperature midway between the solidus temperature and the liquidus temperature, will thus be twice as near to the volume surface of the liquid as it is to that of the crystallized state. Similarly, at the temperature n, which lies midway between m and o, the relative amount of crystals in proportion to the liquid will not be about $\frac{1}{4} : \frac{3}{4}$, but, as the figure shows, it will be about $\frac{1}{7} : \frac{6}{7}$ in the example selected. At the point p,
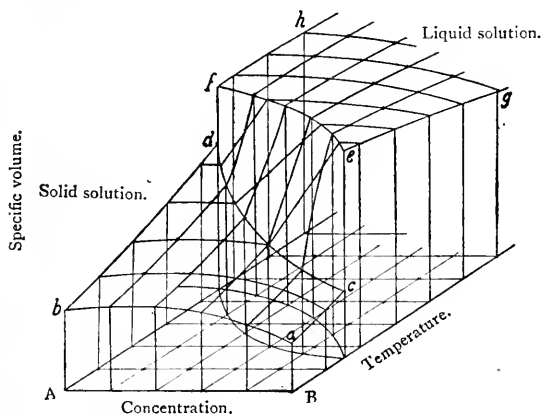
FIG. 1.—Specific Volumes of Alloys forming Solid Solutions.

which lies midway between q and o, and whose vertical distance (temperature distance) from the liquidus ·is three times as great as that from the solidus, it shows, however, in the horizontal interval (concentration interval) the same distance from liquidus and solidus, thus correspond-ing to equal quantities of crystals and liquid. The volume of this mixture must

FIG. 1A.

thus have, at a temperature lying much closer to the solidus than the liquidus, a mean value between the volume of the crystals and of the liquid. By carefully following these arguments we find that in the neighbourhood of A the areas $c\ d\ f\ e$ must curve backward, curving forward on
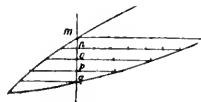
the side of the component B.   Between these two parts
(arched in different directions) of the transition area there is
a straight, inflected line which, projected on the temperature-
concentration axis, gives a temperature horizontal between
liquidus and solidus characterized by the fact of its central
point being equidistant from solidus and liquidus in the
vertical interval.   A typical fact in connection with this
complicated surface is that it can be generated by moving
a straight line in such manner as always to cut through
two points of the volume curves which, when projected on
the base, yield points for liquidus and solidus at the same
temperature.

The case just demonstrated can, of course, at once be
applied to the transformations between two polymorphous,
unbroken series of solid solutions of two metals in each other
of the type which, in common with Tammann, I found for the
cobalt-nickel alloys.

If the melting of one component or the change of the same
with rising temperature is accompanied by contraction instead
of by dilatation, then certain complications arise, the position
now of the volumes of the liquid and of the volumes of the
solid solutions being higher, and the transition surface thereby
assuming a twisted shape.   Since, however, no instances have
previously been known in which such abnormally behaving
metals form continuous solid solutions with other normally
behaving metals, this case is of no actual interest at present.

The next important type to be dealt with is that of an alloy
in which the solubility is complete in the liquid condition, but
limited in the solid state.   Commencing again with the pure
metal A, we first of all obtain a curve like that for the pure
metal A in the first example.   Even the first additions of 20
per cent., &c., are in their behaviour analogous to the corre-
sponding concentrations of the first example, since the limit
of solubility in the solid state is not yet reached.

An alloy with 30 per cent. B lies, however, within the mix-
ing gap of the solid solutions.   The volumes of the hetero-
geneous mixtures of the two mutually saturated crystal types
must show the volume to be a linear function of the composition.
The geometrical solid of the volumes of those mixtures thus

shows an area obtained by moving a straight line from low
temperatures to higher temperatures in such manner that the
projection of such line on the ground plane always remains
parallel to the base line (constant temperatures), the two ends
moving along the volume curves of the two mutually saturated
crystals. The more the expansion coefficients of these two
mutually saturated solid solutions equal each other, and the
lesser the displacement of the saturation concentrations with
temperature, the flatter must be the shape of this area. Con-
versely, it may also assume a very curved shape. Thus we
know that by moving straight lines according to a definite law
it is possible to obtain very curved helical areas.

The lower limits of the volume surface of the liquid are now,
however, formed from two solid curves corresponding to the
two liquidus branches of the two separate types of crystals,
while in the first example only a single liquidus was present.
These two solid curves intersect at a point whose projection on
the base lines is the eutectic point. Since below the eutectic
temperature the volume of this eutectic mixture must rest on
the volume plane of the heterogeneous mixture of the two
mutually saturated types of crystals after passing from the
molten state into the solid eutectic, we can at once get at the
change in volume accompanying the eutectic solidification.
This is shown in a perpendicular descent between the volume
surfaces of the liquid and those of the heterogeneous crys-
talline mixture.

The concentrations to the left and right of the eutectic
point contain, together with primary crystals, relative
quantities of eutectic which decrease as a linear function
of the distance from the eutectic point. The difference
in height of the vertical descent thus decreases as a linear
function of the distance from the eutectic point, disappearing
finally into the extreme points of the eutectic lines. We
thus get a triangle perpendicularly, whose projection on the
ground plane forms only a straight line, while the projection
of the three apexes supply the eutectic point and the extreme
points of the eutectic lines. We thus see the accuracy with
which the investigation of the volume figures gives the
individual curves and points of the condition diagram.

The two separated areas of the volumes of the semi-liquid mixtures between crystals and liquid abut on the two upper sides of this eutectic triangle. These mixtures (as in the case of the former example, with perfect miscibility in the crystallized state) consist, at each moment, of heterogeneous mixtures of crystals and liquid which are in equilibrium at the temperature in question. At a given temperature the volumes of these semi-liquid mixtures must be in every case a linear function of the concentration. In other words, if we erect perpendicular planes on the temperature horizontals of the ground plane, these perpendicular planes intersect the volume planes of the semi-liquid mixtures always as straight lines. The total intersections of these perpendicular planes through the surface of the solid thus yield, above the eutectic temperature, very marked curves consisting of five branches corresponding in order to (1) the solid solutions of B in A, (2) the mixtures of these solid solutions with liquid, (3) the liquid, (4) the mixtures of liquid with the solid solutions of A in B, and finally, (5) the pure solid solutions of A in B. Below the eutectic temperature this great prominence of the temperature intersections at once falls off, and the intersections consist only of three branches which correspond to the two homogeneous solid solutions and their heterogeneous mixtures.

The perpendiculars which can be erected on the concentration verticals of the ground plane, intersect the surface of the volume figure as curves which are also represented in the figure. In this case, however, the volume surfaces of the heterogeneous fields are not cut in straight lines. Especially in the area between liquidus and solidus we get curves whose curvature is still more prominent than in the earlier example of perfect miscibility in the solid state. The figure shows how the total intersections of these planes through the geometrical plane of the solid run first of all as a nearly straight line on the volume surface of the liquid, then, after passing the liquidus branches, rise abruptly and either pass direct on to the volume surfaces of the two types of crystals or, provided the concentration lies between the two extreme points of the eutectics, drop perpendicularly

over the surface of the triangle, and finally continue downwards in the heterogeneous field of the two saturated crystal types.

A concentration of 70 per cent. B would exceed the saturation limit of the solid solution A in B at a definite temperature, consequently entering the homogeneous field without having to pass the eutectic horizontal. Thence onwards, with further rise of temperature, it behaves like the alloys of the example first selected. Passing through the field of the volumes of the semi-liquid mixtures, the volume
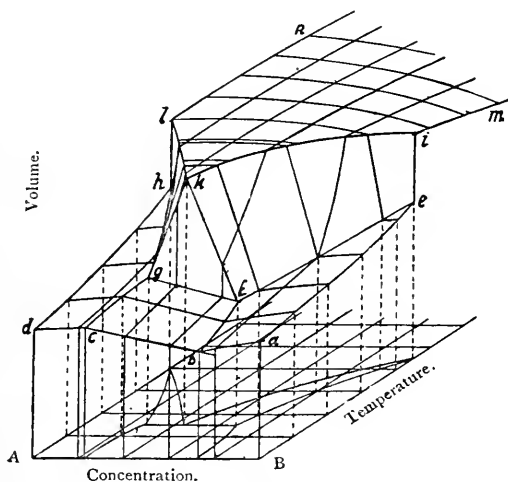
Fig. 2.—Specific Volume of Alloys forming Limited Solid Solutions.

curve finally reaches the volume surface of the liquid, which again has the same shape as in the first example cited.

These few remarks may be sufficient to enable us to understand the entire extent of the volume curves of the individual concentrations of such systems so as to enable them to be utilized for *a posteriori* conclusions concerning the constitution.

We have a variant of this system in cases in which one component melts under contraction. Since such instances occur with bismuth alloys, it appeared useful at least to mention this type. The individual areas of the volume-surface and their significance would be the same as in the preceding case. Since on approaching the pure metal A the volume surface of the liquid

sinks below the level of the volumes of the crystals A, the
volume surface between liquidus and solidus of this crystal-type
A takes a distorted shape, and the maximum sharp descent of
the perpendicular eutectic triangle is considerably less in this
case than in the preceding.   This descent may indeed become,
conversely, an ascent when the eutectic point lies near enough
to the A side, so that at the eutectic point the volume of the
liquid is smaller than that of the freezing eutectic.   It is quite
conceivable, of course, that we may have the fortuitous ex-
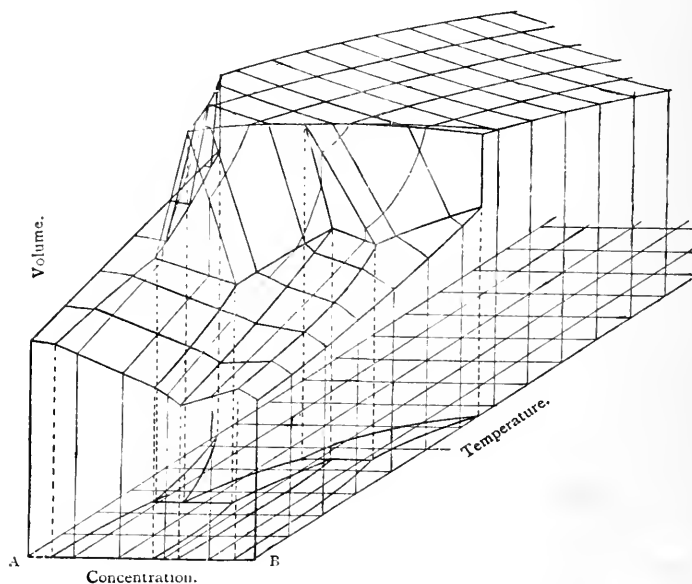
FIG. 3.—Specific Volume of a System containing a Eutectic and Peritectic.

treme case in which the volumes of liquid and eutectic are
practically the same, and we would thus have the special case
in which the eutectic lines were passed without appreciable
change in volume.

The fundamental cases previously cited enable us to under-
stand the numerous combinations of the individual types which
may occur in the many condition diagrams of binary alloys.
A few specially important combinations will now be selected
and diagrammatically illustrated.

We may first of all consider (Fig. 3) as of especial importance the case of a system containing a peritectic (in addition to a eutectic) on which a second type of crystal is formed by a primary crystal type and the liquid. In this case also we get a perpendicular triangle similar to the eutectic triangle, whose projection in the fundamental plane supplies the peritectical with its two extreme points and the peritectic point.
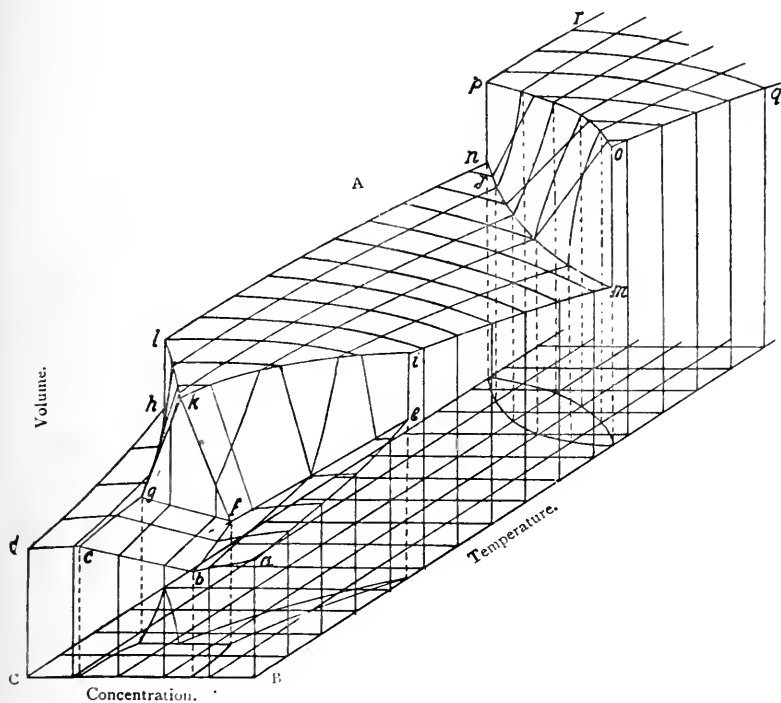
FIG. 4.—Specific Volume of a System with splitting up of Solid Solutions.

Alloys having maximum melting points with definite concentrations can at once be split up into single parts by intersections, called for by the maximum concentration, being afterwards dealt with further by the aid of the types cited in Figs. 1, 2, and 4.

Fig. 2 may also represent the splitting up of a homogeneous solid solution with decreasing temperature into two separate

imperfectly miscible new polymorphous crystalline types
by imagining a third type of crystal to be added in place of
the area of the liquid. These conditions do indeed occur,
for instance, in the case of iron-nickel alloys.   By com-
bining Figs. 1 and 2, by placing them under each other, we
get, united in one figure (see Fig. 4), the transition from the
liquid to the first continuous solid solutions and their splitting
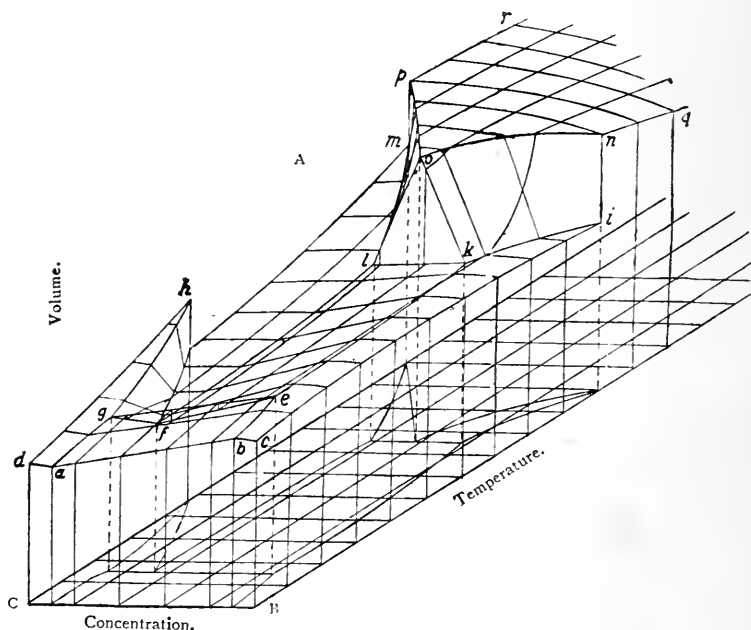
FIG. 5.—Specific Volume of a System containing a Eutectic and Eutectoid.

up into two new crystalline types under the action of a decreas-
ing temperature.

Fig. 5 represents a further case to show the combination of
the process of crystallization with the process of transforma-
tion, by a simple combination of a eutectic with a eutectoid,
in which the one crystalline type splits up eutectoidally into *e*
and *g* with cooling (in consequence of a polymorphous change
into another crystalline type C). Such conditions arise in the
iron-carbon system ; and in order to adapt the facts to the

conditions which actually do exist in this case, we must also assume that the change of the pure crystals A into C on cooling takes place under dilatation. The perpendicular triangle of the eutectoid decomposition of the crystals C has therefore become very flat.

It would, of course, be desirable to extend to more numerous and complicated cases the types previously dealt with; but the examples already given may suffice to introduce the typical shape of the volume surfaces of the alloy, and to give a general idea. What has already been said will also show the advantages of experimental determinations of the volumes as applied to the explanation of the phase-diagram investigation of alloys.

In conclusion, the Author would express his high appreciation of the work done by Mr. Edward S. Hodgson in translating this paper.

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DISCUSSION.

Professor TURNER, M.Sc., Vice-President and Honorary Treasurer, in opening the discussion on Dr. Guertler's paper, said that he was sure they would all receive that paper with pleasure, and it would repay careful study later. He regretted that he had not had an opportunity to carefully consider the figures which Dr. Guertler had given. He noticed, however, that in two or three matters, and on two or three points, what Dr. Guertler had said was entirely in accordance with some practical observations which he (Professor Turner) had made. For example, on page 177, he said : "We thus come to the conclusion that the specific volumes of the pure eutectic must be slightly greater than would be calculated from the values of the pure components by the mixing rule." In a paper laid before the Institute by Mr. Ewen and himself (Professor Turner) two or three years ago, they pointed out that they had experimental evidence for the conclusion that there was a small but still appreciable expansion in connection with the formation of the eutectic. Dr. Guertler also referred to the fact on page 179, "At the melting point expansion generally takes place." He (Professor Turner) understood this to be due to the effect of crystallization. If they had homogeneous liquid, they had the particles packed in the closest possible manner. As soon as those particles began to arrange themselves in a definite crystalline form, there must be some space required for rearrangement. On the other hand, they had the contraction due to the force of crystallization, and so they would not necessarily expect expansion at the moment of solidification to be great. Sometimes it might be almost imperceptible or even negative, but if they imagined for a moment that they had people in that room all packed together as closely as possible, and they were then asked to arrange themselves into some geometrical figure, there must be some increase of space required for the rearrangement, and the people would occupy more space than when closely packed together. That was the condition of things they might have at the moment of crystallization, especially when they were dealing with more than one phase. But he was prepared to grant that in some cases crystallization was associated with contraction. For example, if the metal crystallizes in cubes of equal size and the perfectly packed material were cooling. This was a line of study he should follow with interest, and he was personally grateful to the author for dealing with the subject.

Dr. W. ROSENHAIN, F.R.S., Member of Council, said that there could be no doubt as to the value and interest of Dr. Guertler's paper. It was a theoretical discussion on volume alterations in the various phases which existed in alloys, and it was a discussion on what they might or might not expect to see in regard to volume. That was extremely interesting, but he thought it was necessary to warn readers of the paper that it was purely theoretical, and to a very large extent based upon certain assumptions which had yet to be verified by experi-

ment. They could not even describe it as an attempt to classify the results dealt with, because they had no accurate measurements in relation to volume and temperature over any very considerable range of alloys. The whole of that paper would gain a great deal in value if Dr. Guertler could tell them how to make those measurements. It was all very well to say that theoretically there were two or three ways of doing it, but could they be done? He (Dr. Rosenhain), with his collaborators, had been working at the subject for the last four years, and had been attempting to make those measurements on some such lines as those indicated in the paper. They had obtained a certain number of results, but they were very limited, because the practical difficulty had been insuperable, even with the considerable resources placed at their disposal; in the hope that someone might help them, and help to deal with the subject generally, he would mention what they had done. The method they had adopted was to weigh the alloy in a liquid bath, and to do that they had to get over certain obvious difficulties. They did that by the differential methods—that is to say, they weighed the specimens of alloy against a specimen of copper, working with fairly fusible alloys and employing a short arm balance. The specimens of metal were placed in suitable cups, they were completely immersed in a bath of oil, and then the temperature of the bath was steadily raised. Thermo-couples were placed in the centre of each of the pieces of metal. The temperature of the bath was slowly raised and weighings were taken. That worked very well; while there was a steady expansion or contraction, they obtained gradually changing difference in weight. But the moment there was a critical change they got a change of density on the one side of their balance and no change on the other, and a large change in the difference of weight occurred. They succeeded in getting results within 30 per cent. on either side of the lead-tin eutectic, but they could not carry the process much further, because the oil carbonized and became an exceedingly viscous mixture, and so it was impossible to continue the measurements. It was very evident that to carry out those measurements they must have a suitable liquid. They must have a liquid which would not be seriously affected by the prolonged heating during measurements, and such a liquid was not known to himself or to any of his chemical friends. A bath of molten metal or alloy had been suggested, but there was still some considerable difficulty in the way of preventing inter-diffusion, and altogether the matter was for the present hung up, simply because they had not yet succeeded in hitting upon a suitable liquid. If Dr. Guertler or anyone else could suggest such a liquid that would work, they would have an opportunity of testing the value of those diagrams with which they had been favoured, and in which he was extremely interested.

Dr. GUERTLER, replying on the discussion, said he wished to thank the speakers for their very kind remarks. He was very much interested to hear from Professor Turner that his eutectic mixtures had specific weights slightly different from those calculated by the mixing rule. He

was sorry to say that that fact had escaped his (the speaker's) attention, and he was very interested to hear of it. With regard to what Dr. Rosenhain said, Dr. Guertler stated that investigations really existed giving the changes of volume with temperatures varying from the solid state up to the liquid state, and giving, though not in a very accurate manner, particulars of the transitions from the liquid state to the solid state. He thought if the experimenters had had in mind the theory and the survey of the diagrams he had shown, he believed those measurements would have been carried out somewhat more accurately, but still it was a fact that measurements existed. Many series of alloys could be most easily investigated by the volume method, because there were none of the difficulties engendered by high temperatures. As to the method of realizing those theoretical ideas, he was hoping to get some very good results with tungsten coated with molten silicon dioxide. Tungsten suspended in a molten alloy would lose in weight during the change in temperature. It was possible to determine the specific weight of the alloy by measuring the loss in weight of the tungsten. Of course this method could only be applied to the investigation of liquid alloys. Solid alloys could be investigated by the reversed principle of suspending the alloy in some lighter metallic liquid of known specific weight. It seemed at present rather difficult, but still there were two ways of doing so. One of these depended on the fact that very often liquid alloys could be found which would not dissolve or affect the alloy under investigation. It was, for instance, very easy to study solid nickel in a bath of molten silver, because the two metals would not influence each other, and there were quite a number of combinations that would behave in the same way. Another method was to give the alloy a coating, and that could be done very well with glass. In cases where a glass coating would melt on account of high temperature, one might employ a less fusible material such as silicon dioxide or zircon.

A STUDY OF VOLUME CHANGES IN ALLOYS.*

By J. H. CHAMBERLAIN, M.Sc. (University of Birmingham).

I. Objects of the Research.

Volume changes in castings have formed the subject of research by several authors, while their relation to the equilibrium diagram has given rise to much speculation and criticism. The author therefore undertook the following research on the copper-aluminium series as a continuation of the previous work done on volume changes, with a view to establishing more firmly any relation that may exist between them and the equilibrium diagram ; and he has endeavoured to explain some of the speculations and criticism that have arisen on this subject.

II. Materials Used.

The copper used was very pure electrolytic metal, while the aluminium was the purest obtainable.

The analyses are given below :

	Copper.					Aluminium.				
				Per Cent.						Per Cent.
Copper	.	.	.	.	99·975	Aluminium	.	.	.	.	99·60
Iron .	.	.	.	.	0·023	Iron .	.	.	.	.	0·25
Lead .	.	.	.	.	0·002	Silicon .	.	.	.	.	0·15
Arsenic	.	.	.	minutest trace						100·00
Bismuth	.	.	.	minutest trace				.		
				100·000						

(*Note.*—Copper value above is that given by difference.)

(*Note.*—Aluminium estimated by difference.)

The materials were melted in covered fireclay pots in a coke-fired wind furnace. With the lower percentage aluminium alloys, the aluminium (previously warmed) was added to the molten copper, and the mixture well stirred ; with the higher percentage aluminium alloys, the copper was added in a molten

condition to the melted aluminium, and the mixture stirred
as before.

III. Apparatus Employed.

The method of experimenting was a modification of that
devised and used by Haughton and Turner in their work on
the copper-tin series ([6]).   That is to say the readings of
the galvanometer and the extensometer scales were observed
through one telescope, and were recorded by means of a
chronograph.

The extensometer used, however, was of an entirely new
design, while the author found it necessary to make some
alterations in the mechanism of the chronograph and the
arrangement of the scales.

The Mould and Bar.

These were prepared and made from the same pattern as
that used by Haughton and Turner ([6]).   The bar was T-
shaped, and $\frac{3}{4}$-inch square section, with the object of obtaining
slow cooling, with possible extensometer indications of changes
occurring below " solidus."

The bar was held firm at the T end, which is cast round
a $\frac{3}{16}$-inch iron pin clamped to the box.   The connection to
the extensometer was made by means of a short length of
$\frac{1}{8}$-inch iron wire, with a flattened head, protruding for about
an inch into the mould.

This connecting pin was cooled along the whole length
of the part outside the mould by a spray of water from a
horizontal tube placed above it.

Samples for analysis were taken, when possible, by drilling
the bar through in two places, and where this was impossible
by powdering up a representative sample of fragments of
the alloy in a steel crusher.

Pieces for hardness tests, &c., were taken about three inches
from the T piece.

The Extensometer.

In the paper by Haughton and Turner ([6]) it is stated that
some of the largest expansions observed in the copper-tin

series are produced by forces so small that a slight jamming in the extensometer causes a zero result to be obtained, and as the design and construction of the old form of this apparatus made it rather subject to such friction, unless always connected up exactly in line with the pin from the bar, the author designed and made a more sensitive instrument, in which friction to expanding forces was practically nil. The new extensometer is of the mirror type. A small concave galvanometer mirror is attached to a light strong spindle, poised vertically on needle points, between two glass bearings, both of which are capable of lateral motion, while the top one can be raised or lowered, being adjusted so that the spindle is vertical and moves freely without play.

A small ebonite drum is fitted on the square spindle, the magnification of the instrument being inversely proportional to the diameter of this drum. Round the drum is wrapped, once, a thin silk cord, to the ends of which are attached small leaden weights, accurately counterpoised, which hang vertically and freely over two light frictionless pulleys, P P, on each side of the spindle.

A small oblong bar A lies quite freely on two hollow frictionless rollers, as shown, between two standards. This bar is made in two pieces, a projecting pin on the tail-piece B sliding into a corresponding hole in the main bar A, but by tightening the lever screw S the two parts become rigidly connected. The pin from the casting is joined up to the tail-piece by clamping it in an $\frac{1}{8}$-inch hole drilled in the end. A very small light clamp, attached to a thin rod projecting from the bar A, grips the silk thread at a point between the drum and the back pulley.

To one of the standards carrying the rollers is fitted a small square shaft, working up and down in two bearings; this shaft terminates at its lower end in a V-shaped piece, ground to fit a V-groove cut into the main part of the bar, resting on the rollers. Before the commencement of an experiment this shaft is kept pressed in the groove in the bar, by means of a spring, which holds it quite rigid.

By means of the lever L, shown at the top of the standard, this shaft can be lifted from the bar and is held up by a
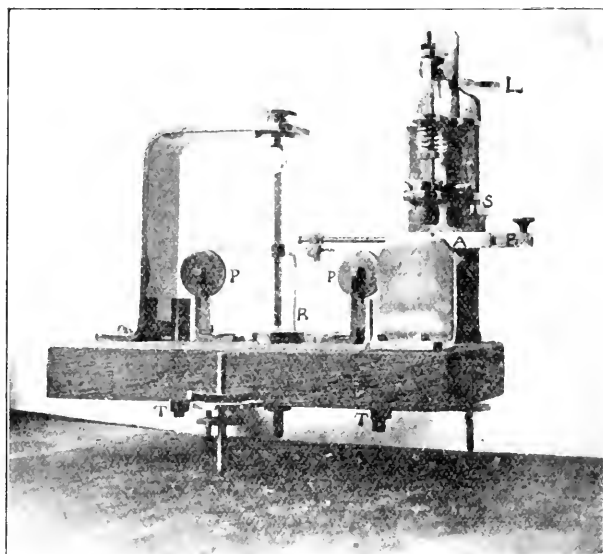
FIG. 1.—The Extensometer.
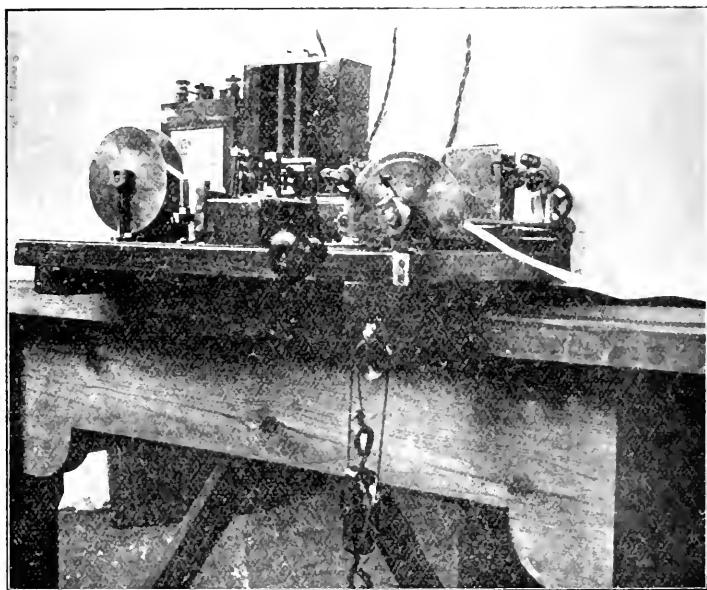
FIG. 2.—The Chronograph.
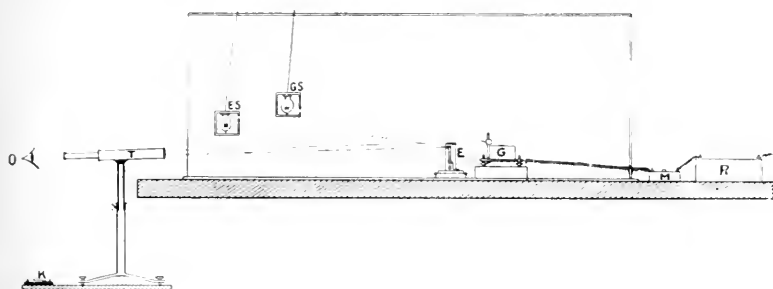
FIG. 3.—Diagram showing the Arrangement of the Apparatus.

small spring catch, and the bar is then quite free to move, its only bearing being the light rollers on which it lies.

The whole instrument is carried on three levelling screws and is adjusted so that the weights hang vertically and freely in the brass tubes T T.

The mirror is attached to the spindle by means of a light aluminium swivel, which allows it to be tilted, so as to reflect the scale in the telescope without altering the level of the instrument.

The system used in experimenting is as follows : the bottom mould is placed in position, and the front pin, connected to the tail-piece B, is put in its place in the mould and adjusted so that it slides freely in and out of the bar A, the clamp S being loosened, and the shaft lowered, keeping the bar A rigid. The couple is then inserted into the mould and the top box put into place.

When everything is adjusted and all the preliminary arrangements completed the clamp S is tightened, rigidly connecting the bar and its tail-piece, and the shaft is raised by pressing down the lever L.

The instrument is now ready to record any expansion or contraction that may take place.

An aluminium pointer R is fixed in the spindle, below the drum, and moves over a small bone scale fixed on to the base of the instrument; by moving this pointer the spindle, with its mirror, may be turned back during an experiment if required, the silk cord sliding on the ebonite drum. By this means therefore one can instantly, and without loosening any

clamps, bring the mirror back on to the main scale should it have been moved by a large quick contraction.

The Pyrometer.

The pyrometer used in the copper-aluminium series consisted of a platinum platinum-rhodium thermocouple, connected through a resistance and mercury switch to a galvanometer. The cold junction was kept in a water bath, the temperature of which was taken before and after each experiment.

The Chronograph.

It was found expedient to make some alteration in the design and construction of the chronograph. A paper tape is drawn through rubber rollers, driven by centrifugally-governed clockwork, and is guided under the three pencils by small rollers. The pencils used are ordinary lead compass pencils, and are clamped into sockets drilled in the ends of three brass levers, arranged one above the other, and pivoted between two upright standards. Three soft iron-armatures are attached to the other ends, and are situated under three electromagnets placed vertically. The armature is of such a weight as to keep the end of the lever carrying the pencil up and above the surface of the paper; on exciting the magnets, however, the armature is lifted off the rest, bringing the pencil down on the travelling strip of paper, marking it with a dot or a dash, at the option of the operator.

The central pencil is brought down, making a dot every second. Another of the pencils is used to register pyrometer readings, while the third registers those of the extensometer.

By using pencils of this kind, they require sharpening only once for about every three experiments, and are easily replaced when necessary by removing the armature rests, thus allowing the levers to be tilted up, the old pencils removed, and fresh ones inserted.

The arrangement of the whole apparatus is shown in Fig. 3.

Both extensometer and galvanometer are contained in a large box painted dead black inside. The galvanometer is placed exactly behind the extensometer and is at a slightly

higher level than that instrument. The scales used are made in the form of two boxes, are translucent, and circular in shape, and illuminated by means of lamps inside the boxes. Both scales can be adjusted for height, and the scale for the extensometer is situated behind that of the galvanometer, so that an observer seated at O may obtain the images of both scales focussed in the same telescope.

As every whole division of the extensometer scale and every half division of the pyrometer scale passes under the cross wire of the telescope, the observer presses one or other of the tapping keys K, thus actuating the chronograph pencils, and so obtaining a simultaneous record on the tape of both temperature and expansion, any maximum reading or any halt being notified by some dot and dash sign on the chronograph tape, and also noted on paper, which the operator keeps in front of him.

PART I.

IV. VOLUME CHANGES IN THE COPPER-ALUMINIUM SERIES.

The bars were cast first in steps of 10 per cent. ranging from pure copper to pure aluminium; other intermediate bars were cast later to fill up the gaps in the rough curve so obtained, the total number being twenty-two. A few typical curves are shown in Fig. 4, while the results of the expansions during the solidification of the whole series is plotted in the form of a curve (Fig. 5), together with the crystallization interval as obtained from Carpenter and Edward's diagram. From a comparison of these curves it is seen that there is a striking similarity between the two. Murray stated that it was possible that the volume changes during the solidification of the brasses were proportional to the distance between solidus and liquidus on the equilibrium diagram. Ewen ([3]) found no such relation in the antimony–lead alloys, but some indications in the aluminium-zinc alloys, which Haughton also noticed in the copper-tin alloys.

The extensometer indications of changes occurring in the alloys after solidification can be noticed in many of the

curves, especially in those of bars 2, 9, and 14, which may be traced to structural changes in the alloy, *e.g.* that of bar 2
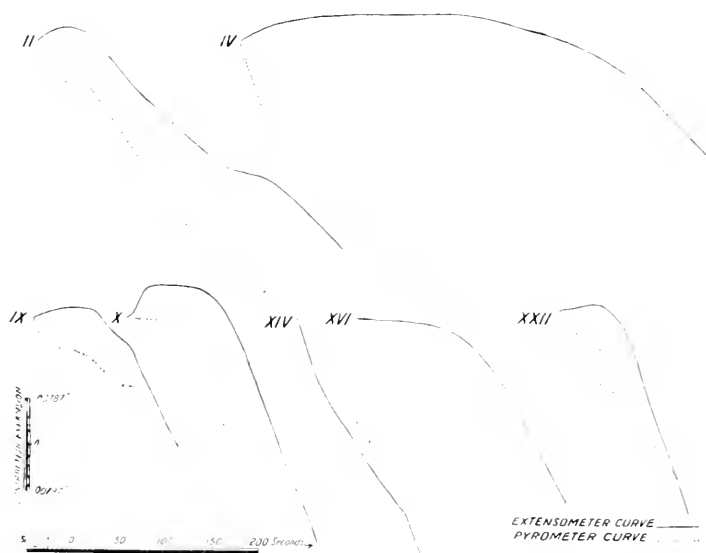
Fig. 4.—Typical Curves showing Synchronous Expansion and Temperature.

occurring about $740°$ C., possibly corresponding to the separation of a' (Cu_4Al) noted in Carpenter and Edwards' diagram,
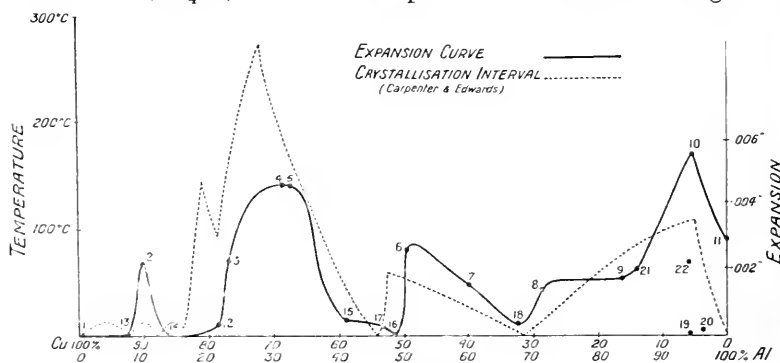
Fig. 5.—Expansion Curve and Crystallization Interval.

while the extensometer curve of bar 9 shows plain indications of both the commencement and the termination of

crystallization, or separation of the eutectic.   Bar 14 shows
an arrest in its contraction curve at about $800°$ C., which
would nicely correspond to the deposition of γ.   Besides
these mentioned there are several more, which, though not
so distinct, may be observed by putting a straight-edge along
the curve.   These extensometer indications below solidus,
however, seem rather isolated, and, as owing to rapid cooling
the pyrometric evidence is unreliable, they do not seem to the
author to deserve detailed notice.

V. HARDNESS OF THE ALLOYS.

This was determined by taking the mean of ten readings
yielded by a Shore scleroscope on specimens from the bars.
The results are plotted in the form of a curve (Fig. 6).   There
is a striking maximum at about 30 per cent. aluminium, thus
suggesting the presence of the compound CuAl; while at
46 per cent. aluminium there is a noticeable minimum which
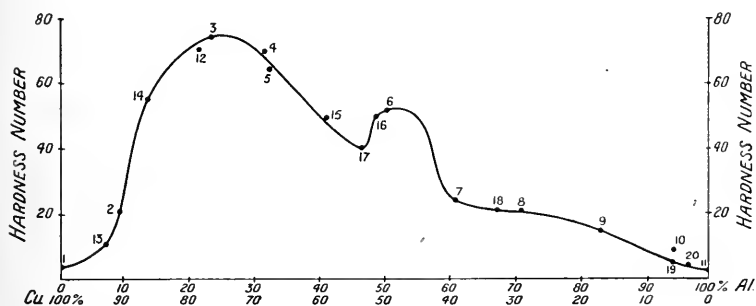
FIG. 6.—Copper-Aluminium Alloys.
Relative Hardness Curve, Shore's Scleroscope.

corresponds with the compound $CuAl_2$.   From this point the
curve rises again to a maximum at about 50 per cent. alu-
minium, which corresponds to the separation of $\delta +$ eutectic.
With the exception of the slight horizontal portion near the
eutectic composition the curve falls regularly to the aluminium
value.   The principles set forth by Kurnakow and Schemts-
chusny ([14]) are well upheld in the main when it is remembered
that owing to rapid cooling the alloys are not in equilibrium.

Below are given the analyses and expansions of the bars, together with remarks as to the condition of the bar :

Bar.	Copper Per Cent. [r]	Expansion in Inches.	Remarks.
1	100·00	Nil.	Rise in gate.
13	92·28	Nil.	Piped.
2	90·27	0·0022	Piped.
14	86·10	Nil.	Piped inside gate. Crystals detachable.
12	78·57	0·00032	Piped.
3	76·85	0·00236	Slight rise. Contained pinlike holes.
4	68·45	0·00472	Gate level. Full of fine blowholes.
5	67·16	0·00472	Gate level. More holes than bar 4.
15	58·68	0·00047	Gate level. Some blowholes.
17	53·60	0·00032	Piped under the gate. A few fine blowholes.
16	51·42	Nil.	Piped under gate.
6	49·75	0·00268	Piped under gate.
7	39·30	0·00157	Piped under gate. Few blowholes.
18	32·60	0·00032	Piped under gate.
8	28·89	0·00142	Slightly piped under gate. Few blowholes.
9	15·90	0·00172	Not piped.
21	13·65	0·00205	Slightly piped.
22	5·86	0·00220	Slightly piped.
19	5·56	Nil.	Not piped.
10	5·40	0·00551	Not piped.
20	3·32	0·00016	Slightly piped.
11	...	0·00283	Badly piped.

From an examination of the two curves, temperature and expansion plotted together, it is to be observed that in every case the general contraction starts to take place almost exactly at the same time that the cooling arrest is over. Hence, with the copper-aluminium series, the volume changes take place " during solidification."

It is interesting to note that the gates of bars 3, 4, 5, 6, and 10, which yielded the largest expansions in the series, have either a slight rise or else are level.   Bars 3, 4, and 5, however, are seen on fracture to contain a large number of pinlike blowholes, which might account for part of the expansion recorded; these latter bars also smell strongly of impure acetylene.

The shape of the individual curves is interesting, because the time duration of the expansions varies very much, lasting in some cases for only twenty seconds, whilst in others for over two hundred seconds.   It has been suggested that the time of duration of these expansions should be taken into account when considering the magnitude of these volume

changes, but an examination of temperature and expansion
curves together leads the author to the conclusion that the
duration of the expansion is proportional to the length of the
solidification arrest, and as this depends not only on the
composition of the alloy, but also on the cooling effect neces-
sarily produced by the mould, which varies with the humidity
of the sand used, it would be almost impossible to attach any
scientific value to the time results obtained under the present
working conditions.

During several of the experiments a slight crackling sound
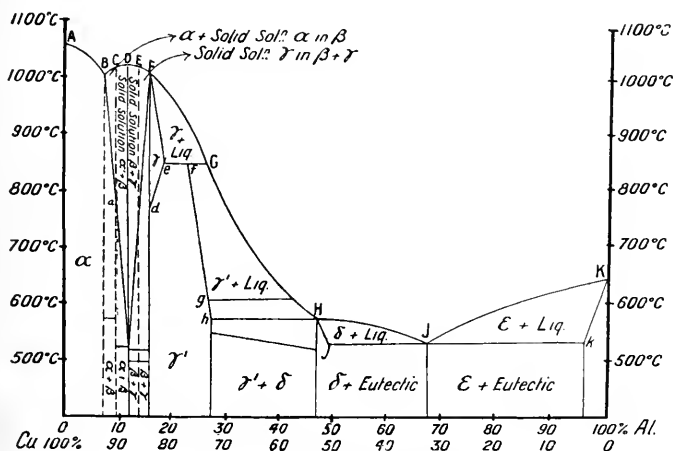
Fig. 7.—Copper-Aluminium Alloys.
Carpenter and Edwards' Diagram.

was heard inside the mould, and at the same time a tremor
was observed, and sometimes a considerable backward jump of
the extensometer mirror was recorded.

On referring to Ewen's paper on aluminium-zinc alloys it
will be seen that the expansion recorded by him on a $\frac{1}{2}$-inch
bar of pure aluminium was 0·00106 inch, while that given by
bar 11 in this research yielded an expansion over twice as
large, viz. 0·00283 inch. To check this result a cast on
aluminium was repeated, and yielded a much lower result
than Ewen's. Again in bars 10, 19, 20, and 22, all very
nearly the same composition, bar 10 yielded a very large

expansion, while bar 19 yielded none, and bar 20 a very slight
one.   Bar 22, which was a recast poured at rather a high
temperature, gave a large expansion, though only half that
given by bar 10.   Wüst, working on alloys, seems at times to
have obtained very varying results on the same material,
e.g. he records for an alloy approximately 90 per cent. copper
and 10 per cent. tin expansions of 0·14 per cent., 0·09 per cent.,
and 0·136 per cent., all as reliable results, while in other places
in his paper a variation of 10 per cent. between results on the
same alloy is recorded.
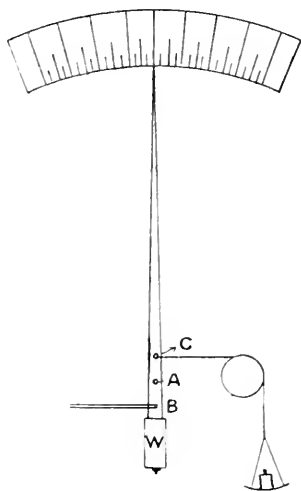
FIG. 8.

The author therefore concludes this part of the paper by
stating that while it is his opinion that with the copper-
aluminium series the expansions during solidification observed
by the extensometer do show a relationship throughout the
series to the crystallization interval of the alloys, they cannot
be considered to possess sufficient scientific accuracy under the
present working conditions to plot the solidus, or to be used
for the purpose of criticizing an existing diagram.   If the
cooling were made much more slowly the extensometer might
give valuable information of structural changes occurring
below the solidus.

PART II.

A STUDY OF VOLUME CHANGES IN GENERAL.

The object of this part of the research was threefold :

(i) To obtain some idea of the force of these expansions.

(ii) To investigate the influence of pouring temperature on these expansions.

(iii) By melting bars to obtain volume changes of the opposite value to those obtained on casting.

The materials chosen to work upon were :

A copper-zinc alloy—about 15 per cent. copper.

A copper-tin alloy—about 90 per cent. copper.

Pure aluminium.

I. THE FORCE PRODUCING THESE VOLUME CHANGES.

It must be understood that the results obtained on this aspect of the volume changes are not conclusive ; lack of time prevented the author preparing the apparatus necessary to give accurate values of the forces producing these expansions.

The old pointer extensometer, used by Professor Turner in his pioneering work on volume changes, was used in these experiments.   A light scale pan was connected by means of a thin strong cord running over a pulley to a hole C drilled in the pointer at a distance from A, the point of support, equal to the distance between that point and B the point of attachment.

Various weights were put on the pan, and a bar cast in the ordinary way, the object being to observe the magnitude of the weight that was necessary to prevent the pin being moved by the volume change.

The results are given in tabular form below :

Bar.			Expansion Observed.	Weight put on the Pan and Lifted.
Copper-zinc alloy	.	.	0·057 inch	700 grammes
Copper-tin alloy .	.	.	0·025 cm.	500 ,,
Pure aluminium .	.	.	0·002 inch	70 ,,

The aluminium result is doubtful as the magnification of the extensometer used is scarcely sufficient to show the change clearly. It is seen therefore that the expansions, both of the copper-zinc alloy and the copper-tin alloy, and probably pure aluminium, are produced by forces of apparently quite considerable magnitude, the exact force being yet undetermined.

II. The Effect of Pouring Temperature on the Expansions.

A sufficient quantity of the copper-zinc and copper-tin alloy was first prepared from the purest materials available, portions of this bulk alloy being taken and melted up for the comparative casts.

The loam used in making the moulds was well mixed and kept in an air-tight bin, so that five or six moulds could be obtained of the same humidity.

The temperature of the metal was taken in the pot before pouring, by means of a Baird & Tatlock direct reading pyrometer. The mode of experimenting was first to try and obtain concordant results, pouring at constant temperature, and then to observe the effect of varying the conditions of casting.

Copper-Zinc Alloy.—The results of the expansions obtained on this alloy are shown in tabular form below, while typical curves are shown in Fig. 9 :

Bar.	Copper per Cent.	Pouring Temperature, Degrees C.	Moisture in Loam per Cent.	Expansion. Inches.
1	16·58	650	9·6	0 1232
2	15·42	740	9·6	0·0861
3	13·95	740	9·6	0·1000
4	13·69	730	9·6	0·0620
5	16·30	790	9·6	0·0586
6	13·86	820	7·8	0·0643
7	13·00	820	7·8	0·0807

Much trouble was experienced in casting this alloy, volatilization of the zinc taking place long before the alloy was

properly melted, causing, as will be seen from the above table, great variations in composition of the bars. In fact it was
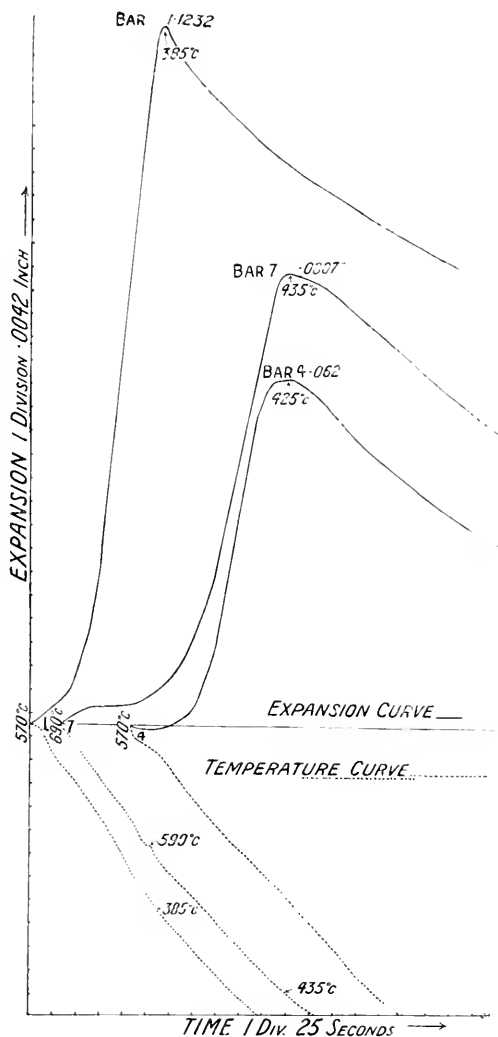
FIG. 9.—Copper-Zinc Alloy Castings.

found impossible to obtain two of the same composition, and as the expansion curve as plotted by Murray ([2]) rises very

sharply in the neighbourhood of this alloy, there is no advan-
tage to be obtained by comparing the expansions of these
bars with each other.   There are, however, several interesting
points to notice about this alloy.

Firstly, it is to be observed that out of seven bars cast the
author obtained three which yielded expansions larger than
any observed by Murray, and it is certain that the maximum
expansion of ·075 inch, which he records for a bar in this
neighbourhood, is not by any means the largest that can be
obtained under suitable conditions ; and it is the opinion
of the author that the higher values obtained in this research
are not entirely due to a difference in composition, but also
to some other influence, which will be dealt with later in
the paper.   A second point worthy of notice is the slight
contraction, or in some cases a slight arrest, which is clearly
shown in many of the bars before the large expansion takes
place.

In all cases observed this first contraction or arrest corre-
sponds with the 590° C. arrest on Shepherd's diagram, the
main expansion taking place between this arrest and a tem-
perature somewhat above 400° C., *i.e.* during the solidification
of the ϵ crystals.

The third point to be investigated was the density of this
alloy, as compared with the density of a chilled specimen of
the same composition, and also with its theoretical density.

An alloy was cast in a chill, and immediately quenched in
water, and after many failures the author succeeded in ob-
taining a chilled alloy of practically the same composition as
that of bar 4.

The analyses showed :

<blockquote>
Bar 4 .   .   .   . 13·69 per cent. copper.
Chilled specimen   .   .   .   . 13·65   ,,   ,,
</blockquote>

As it was found water attacked this alloy, the density ex-
periments were performed in a light oil.

Values were obtained both on lump specimens and fine
drillings, and in the case of each of these experiments were
carried out on both evacuated and unevacuated samples ; the
unevacuated samples were heated in oil until no further gas
bubbles were evolved, while the evacuated samples were left

under the bell jar of an air-pump until no further gas could be extracted.

The density results are as tabulated below :

Lump Specimen.				Drillings.			
Evacuated.		Unevacuated.		Evacuated.		Unevacuated.	
Bar 4.	Chill.	Bar 4.	Chill.	Bar 4.	Chill.	Bar 4.	Chill.
P. Cent. 7·507	P. Cent. 7·44	P. Cent. 7·34	P. Cent. 7·42	P. Cent. 7·52	P. Cent. 7·52	P. Cent 7·43	P. Cent. 7·50

The theoretical density of the alloy calculated on cast copper and zinc is 7·34, *i.e.* a lower value than any obtained above, excepting one. On immersing the samples in oil it was observed that from bar 4 bubbles of gas at once streamed off from numerous points, while with the chilled specimen practically no bubbles were observed. This was made more noticeable by warming the oil or by the use of the air-pump.

In the case of drillings much gas was evolved from each specimen, which was probably only entangled gas.

The evacuated lump samples were taken after the experiment and their surfaces dried ; they were then reweighed, when it was found that the increase of weight showed roughly :

Bar 4 (weighing 50 grammes) absorbed . . . 0·914 cubic centimetres oil.
Chilled specimen (weighing 65 grammes) absorbed . 0·031 ,, ,,

So that bar 4 absorbs nearly thirty times as much oil as the chilled specimen.

A micro-examination of the two bars revealed in bar 4 definite cracks round the crystal boundaries, while with the chilled specimen only crystals of δ surrounded by the chilled liquid could be seen. The chilled specimen was very much tougher than bar 4, while its hardness was 15 as compared with a value of 10 for bar 4, using the Shore scleroscope.

It appears therefore that the expansion observed in this copper-zinc alloy is due in some way to the molecular change between the δ and the ϵ phase at 590° C., and takes place during the deposition of ϵ crystals, and that by this change cracks are produced in the metal. It is owing to the presence

O

of such cavities that the density of bar 4 is found to be less
than that of the chilled specimen in unevacuated specimens,
and in the case of evacuated samples the chilled specimen is
found to have, with drillings the same density, and with lump
specimens, a lower density value than bar 4.   This low value
of the evacuated lump of the chilled specimen may be due to
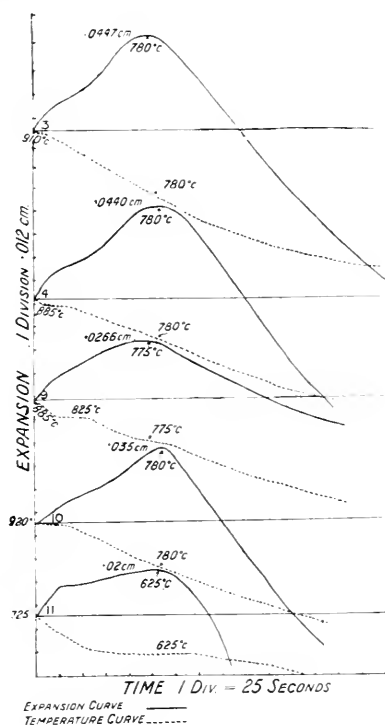
FIG. 10.—Copper-Tin Alloy Castings.

the properly chilled crust being sound and preventing the gas
from being withdrawn from a perhaps more porous imper-
fectly chilled interior.

Copper-Tin Alloys.—Eleven bars were cast in this series,
eight of them in the neighbourhood of 90 per cent. copper.

Typical curves are shown in Fig. 10, while the expansion
values and other information are given in the following
table :

Bar.	Copper per Cent.	Pouring Temp. Degrees C.	Moisture in Loam per Cent.	Expansion. Centimetres.
1	89·95	1122	7·7	0·0374
2	89·95	1122	7·7	0·0374
3	89·95	1200	7·7	0·0447
4	89·95	1200	8·0	0·0440
5	90·40	Above 1200	8·0	0·0300
6	90·40	1190	8·0	0·0400
7	57·60	1170	8·0	0·0153
8	59·10	1165	7·8	0·0230
9*	90·93	1200	7·8	*0·0266
10	90·93	1200	Skin Dried	0·0350
11	60·70	1200	7·8	0·0200

On the whole the results show that by pouring metal of the same composition, at the same temperature, into moulds of the same humidity, expansions of the same value and curves of the same shape are obtained.

It appears that pouring at high temperature leads to larger expansions, but that pouring above 1200° C. diminishes the expansions produced. An examination of the curves reveals the fact that these expansions take place " during solidification," *i.e.* between the liquidus and the solidus arrest, during the separation of the solid solution, the expansion beginning immediately the mould is full.

In practically all cases the curves show a sharp expansion at the beginning, probably due to a chilling effect at the ends of the bar, this being followed by a slight arrest, due perhaps to the slower cooling of the middle of the bar down to its freezing point; after this the expansion goes on sharply to its maximum, this being caused by the rapid solidification of the middle part of the bar.

It should be noticed that a bar cast from a pattern $5\frac{1}{2}$ inches long yielded an expansion considerably over half that given by a bar 12 inches long, though the period of expansion was practically the same.

It is also interesting to note that when pouring this alloy at a high temperature much tin-oxide fume was given off. Bars 7, 8, and 11 were cast to check a zero result recorded by Haughton in his research on the copper-tin series, and were all poured at high temperatures; all these yielded ex-

* Bar 9 was cast from a pattern $5\frac{1}{2}$ inches long, the other bars are all of the usual 12-inch pattern.

pansions. From Haughton's curve a zero result should have been registered for bar 11 instead of the large expansion 0·02 centimetre recorded. The author is fully aware that bar 11 was poured at an absurdly high temperature from a caster's point of view, but the result obtained raises the question at what temperature these alloys should be poured, and he would like to suggest that false zero results are not always due to imperfections in the apparatus, but also to pouring at too low a temperature.

Pure Aluminium.—Twelve bars of the purest aluminium obtainable were cast at various temperatures.

Typical curves are shown in Fig. 11, while the results are tabulated below :
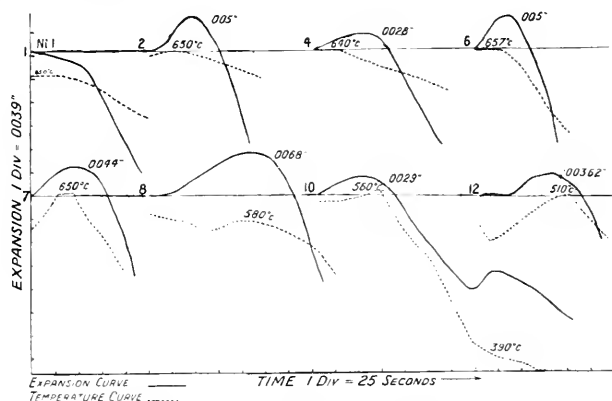
FIG. 11.—Pure Aluminium Castings.

Bar.	Length. Inches.	Poured at. Degrees C.	Moisture in Loam per Cent.	Expansion. Inches.
1 *	5½	790	7·5	Nil *
2	12	790	7·5	0·005
3	5½	790	7·5	0·0011
4	5½	790	7·5	0·0028
5	12	845	7·5	0·0046
6	12	720	8·0	0·0050
7	12	833	8·0	0·0044
8	12	970	8·0	0·0068
9	12	810	8·0	0·0023
10	5½	833	8·0	0·0029
11	12	940	8·0	0·0044
12	5½	940	8·0	0·0036

* The gate of bar 1 showed only slight signs of piping, and was different in this respect to all other aluminium bars cast, which all piped badly.

An examination of the curves and observations during casting reveal the fact that these expansions take place immediately pouring is finished and continue during the solidification of the bar, no expansion taking place after the temperature arrest or after piping is finished.

The irregularities in two or three curves obtained seems to be due to the tendency this metal has to supercool under the casting conditions, while the author is of the opinion that high pouring temperature tends to lead to the observation of bigger expansions, because it allows a short interval of time after pouring before the very quick expansion takes place. When pouring at low temperatures some of the expansion takes place before the mould is filled, so that it is not only unrecorded, but it may also mean that during the observations one part of the bar is contracting and neutralizing the effect of the part poured last, which is expanding.

It is interesting to note the peculiar second expansion in bar 10, accompanied by a temperature arrest at about $390°$ C.

The very rapid contraction of the solid aluminium, in spite of its high specific heat, as compared with copper-tin alloys, for example, is well worthy of notice.

Experiments on the Melting of Bars followed by Slow Cooling.

If the observations which have been recorded are real changes in the volume of the metal in the mould, and are not caused, as has been suggested, by the growth of crystals, which form a chilled shell round the sides of the mould, then on melting a bar a volume change of the opposite nature should be obtained. If, on the other hand, the phenomena are produced by the thrust of metallic crystals growing, one cannot expect to get the reverse change when these crystals simply melt.

Experiments were carried out on the three metals worked on before, viz. a copper-zinc alloy containing about 15 per cent. copper, a copper-tin alloy in the neighbourhood of 90 per cent. copper, and pure aluminium.

The pattern from which the bars were obtained was of the old **T** form, and was 10 inches long and ½ inch square.

Moulds were made from this pattern, bars cast in the usual way, and the expansion and temperature curves taken.

The pin used to connect the bar to the extensometer was of a special design to overcome the possibility of it becoming loose on subsequent heating, and consisted of an ⅛-inch rod, with two small nuts screwed on one end and about a
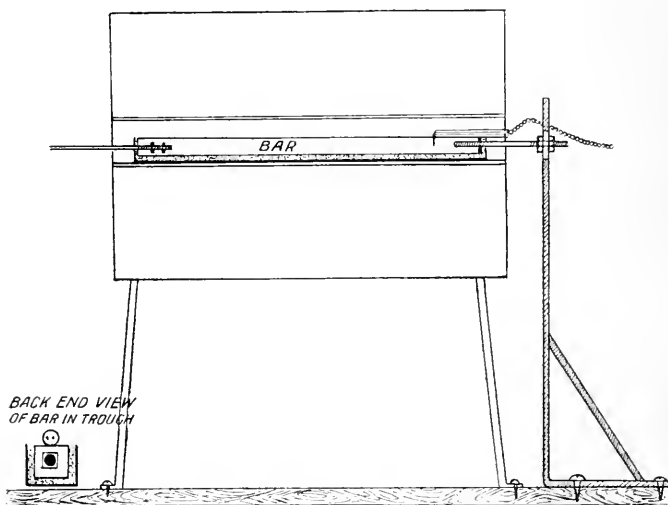
Fig. 12.

quarter of an inch apart; on casting, the metal flows round and solidifies between these nuts, thus assuring a good grip of the pin.

The pin used to hold the other end of the bar firm consisted of a short 3⁄16-inch rod screwed at both ends. This rod was held firm in a horizontal direction by clamping it at one end by means of two nuts through a slot in a vertical standard fixed to the table, the other end, up which a small nut was screwed to act as a chill and take any thrust, projected, as shown in Fig. 12, for a distance of about 1 inch into the long arm of the **T**-shaped mould.

After the various bars had been cast and their expansions obtained, the short arms of the T were cut off, thus leaving a straight ½-inch bar 10 inches long, with the two pins projecting from each end.

The thermocouple wires contained in a short piece of two way clay tubing were bound down on to the top surface of the bar, the junction projecting out of the end being bent over so that it entered a fine hole drilled in the bar about $1\frac{1}{4}$ inches
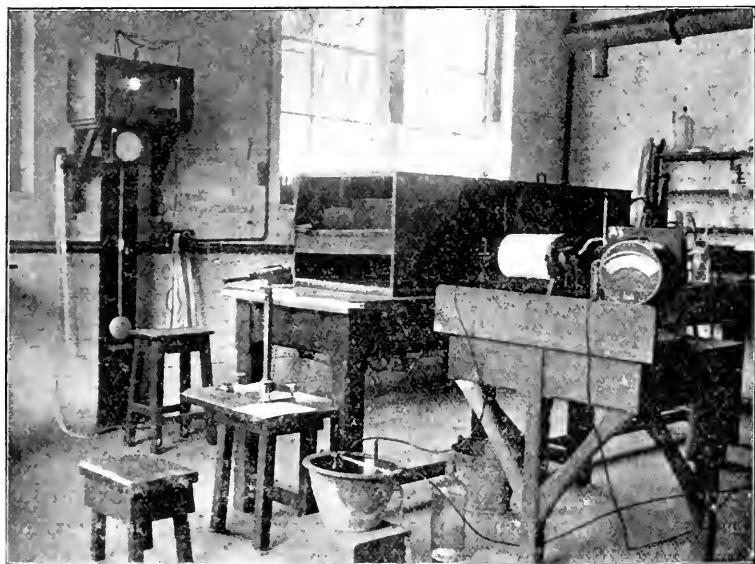
Fig. 13.

from the end. The bar with the thermocouple attached was embedded in loam, in a square-shaped iron trough, so that the bar on nearing its melting point could not sag.

The trough with its bar and thermocouple was slid into its place in a 12-inch Heraeus resistance furnace, the front pin of the bar being connected to the extensometer, the back one being clamped in the vertical standard screwed to the table.

The ends of the furnace were covered with mica windows.

The current could be regulated by means of a resistance placed close to the observing telescope (Fig. 13).

As the furnace was heated up the bar rose in temperature and expanded at a rate sufficiently slow to allow readings to be taken with ease without the use of the chronograph.

After heating the bar to the melting point and taking observations the current was switched off and the bar allowed to slowly cool, readings again being taken.

Copper-Zinc Alloy.—The results obtained on a copper-zinc alloy, containing 15·29 per cent. copper, heated up and cooled down five times in the electric furnace in the manner described above, are tabulated below, while typical curves are shown in Figs. 14 and 15 :

Operation.	Heating Up.			Cooling Down.		
	Contraction.	Temperature at which Contraction Began.	Temperature at which Contraction Finished.	Expansion.	Temperature at which Expansion Began.	Temperature at which Expansion Finished.
	Inch.	Degrees C.	Degrees C.	Inch.	Degrees C.	Degrees C.
1	0·0113	415	470	0·28	570	410
2 *	0·0335	420	495	0·09 *	500	...
3	0·0330	450	515	0·119	540	445
4	0·0099	425	480	0·09	530	435
5	0·0026	470	505	0·091	590	450

From the curves and table it is clearly shown that on heating there is considerable contraction of the bar during a range of temperature, probably corresponding to that on Shepherd's diagram, indicating the solidification of the ϵ crystals ; this contraction is followed by an expansion, which is continuous until the bar becomes liquid.

On switching off the current and allowing the bar to slowly cool first a contraction is noted, followed by an arrest, and then by an enormous expansion taking place between temperatures of $590°$ C. and $430°$ C., *i.e.* during the solidification of the ϵ crystals. While the bar was expanding it was hard and solid to the touch. Subsequent heatings of this same bar all revealed considerable contractions, though they seem to diminish in value each time. Large expansions were

* The expansion obtained on cooling down the second time could not be registered to its maximum, owing to a derangement of the apparatus by the previous large expansion.

also obtained on cooling the bar the second and following times, though here again smaller values were obtained as the operation was repeated. During the heating up of bars of this alloy small globules of metal liquated out on to the top surface of the bar, and there were indications of some bursting, for they were found adhering to the top of the furnace tube. After the fourth heat of the bar a lump of metal (yielding 13 per cent. copper), weighing over 10 grammes,
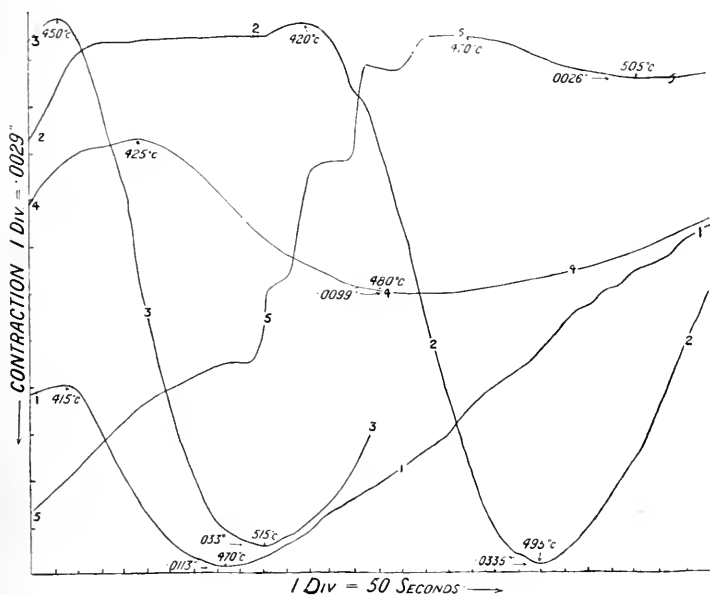
FIG. 14.—Copper-Zinc Alloy Heating up in the Electric Furnace.

was found in the bottom of the furnace, though there was no visible sign on the outside of the bar to show whence it came.

It will be noticed that the expansions observed on cooling down this bar are far larger than the contractions which take place on heating up, and after the fifth heat the bar was found to have grown in length by $1\frac{1}{2}$ inches and now had an average cross-section as shown in Fig. 16.

On fracturing the bar in several places it was found to be piped with a fine hole running down the centre. The metal

left in the centre of the bar round the piping hole, and also
to a small depth from the surface, showed signs of oxidation.
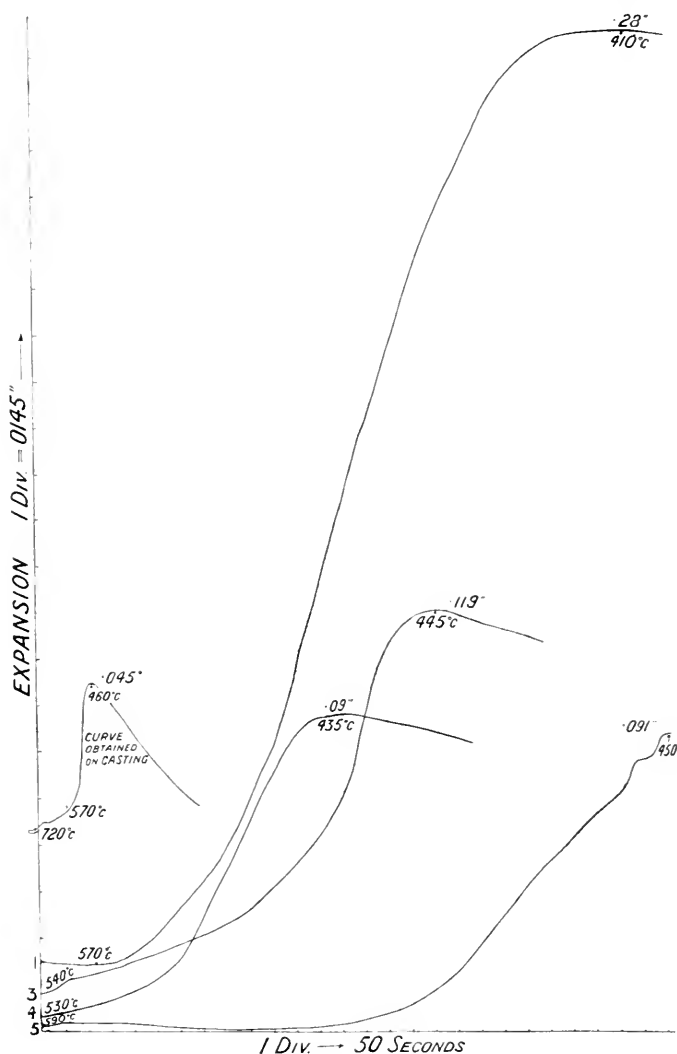
FIG. 15.—Copper-Zinc Alloy Cooling in Electric Furnace.

A photomicrograph reveals the rotten state the metal has
acquired during these operations (see Figs. 17 and 18). It

has been suggested to the author that the growth of the bar is a similar phenomenon to that which can be observed in cast iron ([16]), but although the signs of oxidation noticed, the bowing of the bar, and the change in cross-section would at first suggest such an explanation to be true, the fact remains that on heating up the bar no growth is obtained, but a slight contraction, while on cooling through the same period, the same opportunities for oxidation being present, the growth takes place. The author ventures to suggest the following explanation.

Gulliver states that in alloys in the neighbourhood of 14 per cent. copper : on annealing, the ε crystals are capable
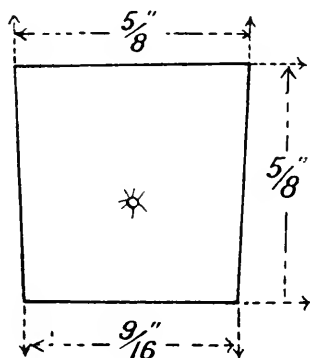
FIG. 16.

of dissolving primary δ crystals, leaving cracks in the metal. After casting a bar, the δ first formed cooling down to 590° C. indicates a slight contraction or an arrest. At 590° C. there is a change from the δ into the ε constituent, and between 590° C. and 440° C. the ε crystals absorb some of the δ variety, leaving cracks in the metal, and, owing to the absorption taking place and the change of crystalline structure, lead to the expansion recorded (see microphoto, Fig. 17).

On heating up liquation occurs in the ε crystals, the liquid running into the cracks produced by the previous operation, the skeleton crystals left intertwining, so causing a diminution in volume. Above 590° C., when the metal is in the δ phase, expansion goes on in the usual way with rise of temperature.

On cooling the first portions to solidify are the sides, and especially the top surface, which gradually reach the ε stage, the middle and lower part of the bar being still δ; the ε crystals and liquid on the outside use their power of solution

FIG. 17.—Copper-Zinc Alloy as cast.
Copper, 15·29 per cent.   Lightly polished.
Magnified 100 diameters.
Note structure just appearing, and also the cracks and cavities in the metal.

on the δ and so remove some of the metal from the interior of the bar, leaving distinct signs of piping along its centre, and as they cool and separate out in their particular crystalline form, expansion is again produced. The observed fact that the contractions tend to become less pronounced as the

operations are repeated may be accounted for by the more homogeneous state the crystals obtain by the repeated anneal-ings; while the diminution observed in the expansions on
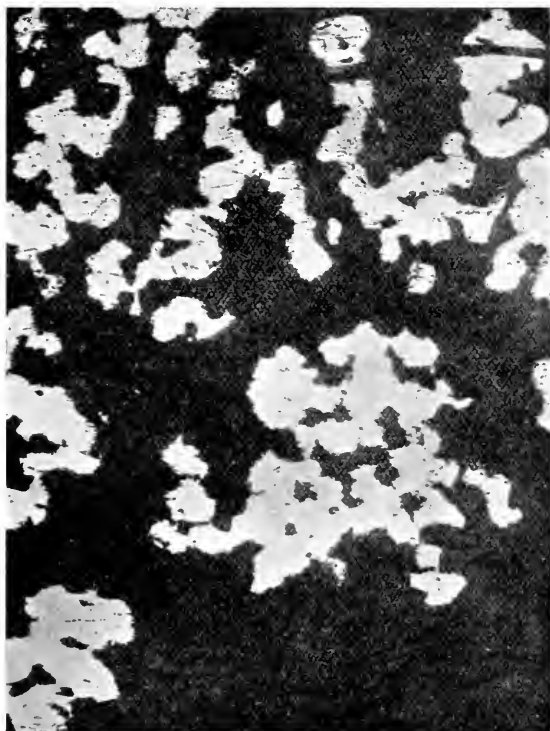
Fig. 18.—Copper-Zinc Alloy.
Copper, 15·29 per cent.
Heated up and cooled down five times in the electric furnace.
Lightly polished.
Magnified 100 diameters.
Metal—white : Cavities—black.

cooling might be traced to the fact that after the first opera-tion there is some accommodation provided in the porous metal itself for the subsequent expansions, so that only a part of their value is indicated in the change of length of the whole bar.

Copper-Tin Alloys.—For comparison the result of three bars are tabulated below and their curves shown in Fig. 19:

Bar.	Copper per Cent.	First Heating.			Second Heating.	First Cooling.	Second Cooling.
		Contraction.	Temperature at which Contraction Began.	Temperature at which Contraction Ended.			
		Centimetres.	Degrees C.	Degrees C.			
D	89·6	0·012	700	760	Bar parted in two in first heating.		
G	89·7	0·00015	930	950	Normal expansion	Normal tion.	contrac-
J *	91·0	0·00045	795	810	Normal expansion	Normal tion.	contrac-

FIG. 19.—Copper-Tin Alloys Heated up and Cooled down in Electric Furnace.

Great difficulty was encountered in getting anything like uniform melting of the whole bar, and it is for this reason

* Bar J was cast 9 inches long instead of 10 inches so that its heating and cooling in the furnace might be made a little more uniform.

that the pyrometric results of the bars are in some cases so low, the back ends of these bars being the last to melt. It will be seen that in bar D a definite and considerable contraction was obtained on heating, followed by an expansion, which went on and was indicated even after the bar had become liquid.

On cooling no expansion was observed, but a contraction, which was quite uniform. Bars G and J did not show such marked contractions, though longer arrests were obtained, but as the author was compelled through circumstances to use a wider furnace for the melting of these two bars the heating was not so uniform as in the case of bar D, and it is his opinion that the long arrests with low contraction results are due to the opposition of the contracting hot central portion and the cooler expanding ends.

In all cases on cooling down only uniform contraction was obtained, and subsequent heatings now failed to produce contractions. These results, and indeed the phenomena observed in casting, suggest that the expansions produced are due in some way to the effect of the cold mould chilling the liquid solution between the dendrites of the solid solution a.

Heating up or annealing the bars leads to homogeneity of the a crystals, and more complete solution, causing a contraction of volume.

Pure Aluminium.—The results on bars of this metal were highly satisfactory and are tabulated below. Curves are shown in Fig. 20.

Operation.	Heating Up.			Cooling Down.		
	Contraction.	Temperature at which Contraction Begins.	Temperature at which Contraction Ends.	Expansion.	Temperature at which Expansion Begins.	Temperature at which Expansion Ends.
1	Inch. 0·0032	Degrees C. 680	Degrees C. 730	Inch. 0·00355	Degrees C. 745	Degrees C. 685
2	0·00276	690	725	0·00348	750	690

These experiments satisfied the author that in aluminium at a temperature range above and during its melting point·

there is a change in volume which is indicated by an extensometer, for it was found that within that temperature range either a contraction or an expansion of the bar could be obtained at the will of the operator, in the one case raising, or in the other lowering, the temperature of his furnace.   It is
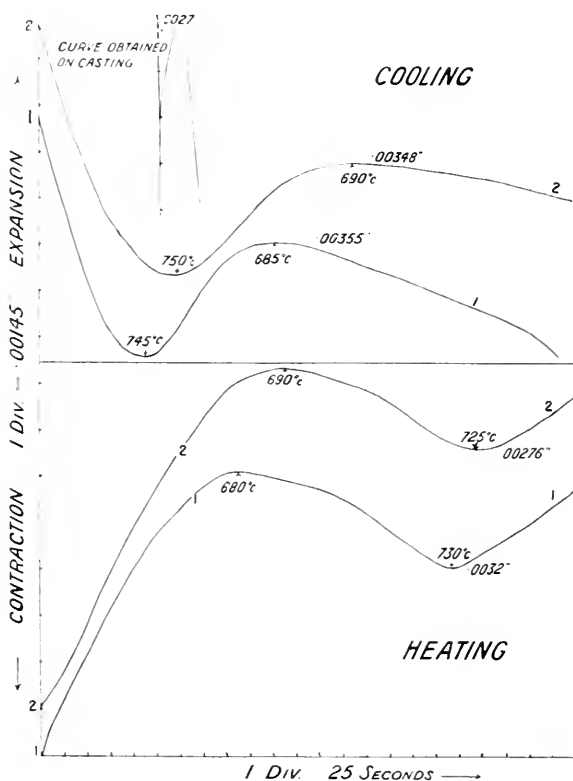
FIG. 20.—Pure Aluminium Heated up and Cooled down in Electric Resistance Furnace.

worthy of notice that in the case of aluminium the contraction and the expansion observed are very approximately equal in value and seem to occur over a definite temperature range.

Since in casting the expansion is accompanied by piping, it seems impossible that it is due to a change in the pure liquid metal, which shrinks before solidification, causing the

piping. It is possible, however, that it is caused by impurities, perhaps by a gas existing in solution in the liquid aluminium, but which separates out between the crystals as they become solid in the form of a compound, causing an expansion. This is evidenced by the fact that a small, yellow deposit was observed on the inside of the hollow gates in many of the bars, which may possibly be aluminium nitride.

On melting the metal the gaseous impurities may again go into solution, causing a diminution in volume.

It is interesting to note that the extensometer will register expansions and contractions even in the liquid aluminium (see curves, Fig. 17).

Summary.

1. The expansion curve obtained on casting a series of copper-aluminium alloys shows a distinct relationship to the crystallization interval curve.

2. The expansions are produced by forces of considerable magnitude.

3. The extraordinary large and quick expansions, peculiar to copper-zinc alloys in the neighbourhood of 15 per cent. copper, are always preceded by an arrest; the expansions only taking place during the crystallization of the ϵ variety.

4. Microscopic examination and density experiments revealed cavities round the crystal boundaries of this copper-zinc alloy. They are produced by the absorption of δ by ϵ crystals.

5. With copper-tin alloys (90 per cent. copper), and with pure aluminium castings, the temperature of pouring has an effect on the expansions observed.

6. Bars of a copper-tin alloy (90 per cent. copper), a copper-zinc alloy (15 per cent. copper), and pure aluminium, all indicate a contraction while being slowly heated up to their melting points, which suggests that the growth of the chilled shell first formed cannot be responsible for all the expansions observed on casting.

7. The contraction of the copper-zinc alloy, when slowly heated, may be due to the liquation of ϵ crystals, the liquid

filling up the cracks in the casting, the skeleton crystals left intertwining.

The large expansion and the continued growth of the bar on repeated heatings may be due to this filling up of the cavities, followed by the crystalline change from δ into ϵ.

8. With the copper-tin alloy (90 per cent. copper) the expansion is apparently produced by the chilling of the liquid round α dendrites, since it is not observed when once the bar has been annealed.

9. With aluminium the volume changes observed on heating and cooling are probably due to the presence of some gaseous impurity.

In concluding this paper the author ventures to hope that the phenomena of volume changes, the study of which was begun at the University of Birmingham by Professor Turner and continued by many of his students, has been investigated a little more fully in this research, and that either himself or some other past or present student at Birmingham will have opportunity of carrying out further experiments with better methods of uniformly heating the bars and more trustworthy pyrometric results.

The author wishes to express his thanks to Professor Turner for his supervision and great freedom of action permitted, to Mr. Hudson for his advice and encouragement, to Mr. J. L. Haughton for explaining his method of working, and he is also indebted to Mr. J. Ward, the University steel melter, for his willing help in pouring the metals and reconstructing the chronograph.

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DISCUSSION.

Dr. W. GUERTLER (Berlin), in opening the discussion, said that the theoretical part of the paper was based on somewhat different lines to those dealt with in his (the speaker's) paper.   He could not help believing that the method employed by him—really an old method—was more reliable.   This method would give the volume independently of the time, while the other method, being dependent on the variations of time, would give varying results.   The dependence of volume on time could not be given in a certain formula which would definitely appertain to and characterize each alloy and always be strictly reproducible. The formula would be undefinable and uncontrollable, because in it the volume really depended on the change of temperature, and that again depended upon the cooling effects and the different heat effects which occurred during the cooling process, and would influence the volume curve in an uncontrollable manner.   One could never tell exactly if a certain irregularity of the cooling curve were really due to a volume change, or to a change in the rate of cooling only.   But given the dependence of volume on temperature, one would obtain absolute values which could always be reproduced, and with the absolute values of a whole series of alloys one could construct the volume surface of absolute and permanent validity.   In cooling or heating experiments, one would have to move the temperature too quickly to reach complete equilibrium, and the results would depend on the more or less near approach to the equilibrium.   On the other hand, his (Dr. Guertler's) method enabled him to maintain a constant temperature for any given time, until equilibrium was insured and a definitely valid volume-value obtained.   This tri-dimensional volume-diagram showed the volume of every single alloy at any given temperature, and included also the volume changes, which could be found during the cooling process, provided they knew the temperature.

Mr. O. F. HUDSON, M.Sc. (Birmingham), said he had read that paper with very much interest, and he thought Mr. Chamberlain was to be congratulated on the way he had attacked a very difficult problem.   He had attacked it on the right lines in studying the conditions likely to influence the results obtained with the apparatus he had used.   He (Mr. Hudson) had been able to see this work in progress from time to time, and he would like to bear testimony to the large amount of trouble taken with the experiments, and the ingenuity displayed in making that apparatus as efficient as it could possibly be.   There was one point that might perhaps have been more fully explained in the paper, and that was the correlation of volume changes with crystallization intervals. The results in the paper seemed to be rather contradictory, particularly in the case of the copper-tin alloys.   In the case of the copper-tin alloys which he used, the author showed that considerable expansions were registered when the alloys were cast under ordinary conditions. When, however, the bars were subsequently heated to the melting point and slowly cooled, no expansion was observed.   This appeared to make

it difficult to regard volume changes as a measure of the crystallization intervals of these alloys. The expansions observed appeared to depend entirely on the conditions of casting, such as pouring temperature, rate of cooling, and condition of the mould.

Professor T. TURNER, M.Sc., Vice-President and Honorary Treasurer, said that he would like to bear testimony in the first place to the skill and patience which had been shown by Mr. Chamberlain in that investigation, and also to the independent line of study which he had adopted in the second year of his work. The first year was practically entirely devoted to the aluminium series. After that he was given a free hand to consider some objections that had been raised to the method, and as far as possible to ascertain the truth. The suggestion that they should ascertain volume changes by heating any alloy as suggested by Dr. Rosenhain was naturally one that presented itself to them in the early part of their investigations, and they made some preliminary tests in that direction, though not of course with the refinement that Dr. Rosenhain had mentioned. They made their tests in oil at a temperature not above 400° C. ; but with an alloy of higher melting point, when they began at 500° C., and went up to 1100°, the oil decomposed and that method, as far as they were concerned, was out of court. He would, personally, be much interested to see the results of observations of any other persons who could introduce revised methods. But they could not wait until a perfect system was introduced, and as the matter appeared to them urgent they adopted the method which had been described, and he ventured to suggest that they made very definite observations, the accuracy of which could not be impugned because they had been confirmed by such observers as Keep, Wüst, and a number of others, besides various workers operating independently in his (Professor Turner's) laboratory. For example, an alloy containing about 15 per cent. of copper expands in an extraordinary manner in the mould, yet so far as he was aware this fact had not previously been recorded in scientific literature. In a paper given by Murray, it was shown that the curve was very steep at the very point of maximum expansion, and that was the reason why Mr. Chamberlain was not able definitely to obtain the exact peak of that curve. The difference of only $\frac{1}{10}$ per cent. in the proportion of copper made a very great difference in the expansion. When they had a curve which went up to a peak in the diagram in that way they would realise how great that expansion was. The results of all Mr. Chamberlain's experiments would lie on or very near to that curve, but they were not sure yet whether they had quite got to the peak. It was at one time suggested that perhaps those observations had to do entirely with crystal thrust, and the outside of the casting was expanding, and that the liquid metal filled up the space, so that there was no real expansion of the material itself. They had first to consider that objection, and they approached it in two different ways. First, they took a sample of the fluid metal, and chilled it in water, and they allowed the remainder to slowly cool. Then they took the density of the

two materials, and found that the slowly-cooled material had a distinctly smaller density. So far, then, as the density observation was applicable in that case, they considered they had ample proof.

The next proof consisted in the extension of the length of the bar. If they took a bar 1 foot long they found it extended in length by 1·5 inches, so that a bar of 12 inches long became $13\frac{1}{2}$ inches long, and by the time they had finished it was extended not merely in length but in width and depth. If they took the diagram on p. 219, that was originally a half-inch bar. It had become five-eighths of an inch in width, and five-eighths in height, so that, taking the most remarkable of their expansions, and examining them in that way, they said that this was not a crystal thrust at all, but that those expansions took place while the material was so solid that it could be handled as a bar.

The matter was confirmed again by putting that same cooled bar into an electric furnace, and heating it up slowly. The heating was done very slowly, so that it would take some minutes to pass through a few degrees. After taking the bar up to a certain temperature below its melting point, and then allowing that solid bar to cool, it expanded, and continued to expand during cooling, and the expansion was even greater than was shown in those bars of cast iron which Professor Carpenter mentioned on previous occasions. In the diagram shown on p. 221, all the black portion consisted of holes, and the white material was alloy. They could understand, therefore, why the bar as a whole expanded. That was not, of course, strictly speaking, a volume change in the sense in which that term was used by Dr. Guertler, because, from his point of view, he took the density from the white part, but from the point of view of a practical man if he wanted to know the size of his casting he had to take into consideration those spaces. So much, then, for the typical case of the highest expansion. An entirely different kind of expansion was observed where they had a solid solution. Here they had a cored structure, where first of all one part of the metal, the original copper rich dendrites, behaved differently from the poorer portions which crystallized out afterwards. During the crystallizing interval they had in that case the expansion, first recorded by Keep, and confirmed by Wüst, by themselves and others. If they took the same bar, and put it into the electric furnace, and heated it gradually, the expansion was reversed, and so they had contraction while the material was being thoroughly annealed. As soon as the material was thoroughly annealed, so as to make it uniform in structure, if they put it in the electric furnace, and heated and then cooled it, it behaved as uniform material, and there were no further expansions or contractions other than the uniform variations due to change of temperature. These were two distinct and different cases, and now there was a third case, which perhaps corresponded with what was suggested by Dr. Desch. That behaviour only occurred in a limited number of cases with pure metal. In the case of aluminium there appeared to be an expansion of the crystal envelope, the outside liquid was drawn in and filled up the spaces, and as soon as that liquid was all solidified then the aluminium ceased to expand.

He did not contend that the extensometer method was strictly scientific and accurate, for the elucidation of difficulties with the equilibrium diagram, as was to be inferred from the paper by Murray.   It might yet prove to be so as a result of further experience.   But in the absence of a better method he suggested that most interesting results had been obtained, and those results had been presented in a series of papers to the members of that Institute.   For the moment they were prepared to leave that subject, considering that they had done their share in that investigation.   If any critics or any friends—and he hoped that the friends and critics were only two names for the same kind of people— thought they could see any better system, or devise any method of their own for the purpose of carrying on that investigation, no one would read their papers with more interest than himself, and the students who had worked with him.

Mr. H. I. COE, M.Sc. (Birmingham), said that he could not venture to criticize the paper which had involved so much hard work.   There were, however, two or three points to which he would like to call attention, one of which had already been mentioned by Mr. Hudson.   He thought Mr. Chamberlain had taken a great step forward in studying the conditions existing in the bar itself.   Hitherto he rather thought that some of Professor Turner's students had devoted too much time to devising apparatus which would measure very accurately something in itself uncertain.   But Mr. Chamberlain had started by considering the variable conditions existing in the bar, and by taking the volume changes on heating, and had thereby confirmed very well, he (Mr. Coe) thought, the fact that there was a contraction on melting corresponding to an expansion on solidifying.   He would like to make one or two remarks with regard to the causes of expansion.   Some had suggested that crystal thrust alone was responsible for the expansion on solidification.   On the other hand, it was implied in the first paper read before the Institute that the extent of the expansion was controlled solely by the crystallization interval.   He was of the opinion that neither the crystallization interval nor the crystal thrust was solely responsible. The evidence he had to offer had been obtained by him through the study of volume changes in certain iron carbon alloys.   One part of the research consisted in adding manganese to pure cast iron.   The white iron showed no indication of expansion on solidification, but the addition of manganese up to about $2\frac{1}{2}$ per cent. caused an expansion. Then the expansion gradually fell off until, in the presence of 5 per cent. of manganese, there was no expansion.   In that case the micro-structure was identical in all cases, showing primary crystals embedded in eutectic, and in all cases the crystallization interval was practically identical.   He would like to draw attention to a practical point in connection with the study of volume changes.

He knew of one firm of engineers who had found it financially more satisfactory to give up the production of iron castings in favour of aluminium zinc castings.   They had difficulty, however, owing to the

cracking of many of these castings during or just after solidification. They could not trace the cracks to any fault in the design of the pattern, and that was probably one of those cases where a close study of volume changes might enable serious loss, due to cracking, to be eliminated.

The PRESIDENT (Professor A. K. HUNTINGTON, Assoc. R.S.M.) said that he thought this paper was a most valuable paper, and they ought to welcome it as breaking, to a certain extent, new ground, and he was sure it would help them to get a better grasp of the subject. They had had so many papers on micrographic work that they would welcome the breaking away into other physical directions. He considered that direction of the utmost importance from the practical point of view. Things which had come within his own knowledge, comparatively recently, had impressed him very much with the necessity of work in this direction, and they realized that there was a good deal of difficulty in carrying out experimental work. Nevertheless their work was to take up those problems and difficulties, and deal with them one by one. He was quite sure the Institute would welcome work in that direction, as likely to prove of very great practical value, and that specially applied to the paper before them.

Mr. CHAMBERLAIN, replying on the discussion, said that Dr. Guertler had mentioned the irregularities, remarking that heating up and cooling down the bars might possibly cause irregularities in the contraction. That was so, and could be easily traced from the preliminary experiments. But he did not think there was very much wrong. He was hoping in the further research to improve the apparatus and the method for heating and cooling those bars, and so keep the temperature more constant.

With regard to Mr. Hudson's remark about the second part contradicting the first, he did not think that was so altogether, though he admitted that it rather tended to prove that the first part was not quite so reliable. That volume changes in castings did show some relation to the crystallization interval could not be doubted. As to why that was so, he was afraid that at present they could not definitely say. But it seemed a quite reasonable conclusion to draw, that with copper-tin alloys the expansions recorded on casting were due to the chilling effect of the mould. And that chilling effect might be most pronounced when the crystallization interval was at its maximum. It was quite clear that more work must be done in that direction before they attempted to say what caused that expansion. and why they apparently bore such a marked relation to the equilibrium diagram crystallization interval. Professor Turner rather led them to suppose that the volume changes in aluminium might be due to crystal thrust. He could not for a single second believe that.

He had, however, himself found that the expansion in aluminium

took place before and during solidification, and that no expansion was recorded after piping was ended, and a year ago he felt very strongly, and even went so far as to state in a thesis he then submitted to the Birmingham University, that volume changes in aluminium were probably due to the crystal thrust. But since then he found, as he had stated in the present paper, that on melting a bar of aluminium, a definite contraction could be obtained, although the temperature of the bar was being raised ; and although one could understand an outside shell of chilled crystals being formed round the sides of the mould, growing and exerting a thrust, it was impossible to conceive of those same crystals causing a contraction by simply melting. With aluminium the phenomenon was purely and simply a volume change of the whole bar.

Professor Turner seemed to imply that the work was finished. For his (Mr. Chamberlain's) part, he thought it was only just begun, and he was hoping to go on with it for some years to come. But he intended to make a few experiments *in vacuo* to prove certain points which were still in doubt. He was very grateful for the kind words which had been spoken, and which had been extremely encouraging to him, and he had every hope that he might be able to continue the work.

The PRESIDENT said he would like to endorse the concluding remarks of Mr. Chamberlain, and express the sincere hope that Professor Turner was not going to give up the work. In fact, in a little conversation at the table he had been strongly urging Professor Turner to arrange for this work to continue. Professor Turner had made that his own line of research, and no better person could possibly be found to handle it. He really hoped that the matter would be reconsidered.

COMMUNICATION.

Mr. J. L. HAUGHTON, M.Sc. (Teddington), wrote that he had read Mr. Chamberlain's paper with great interest, especially as he had had the pleasure of seeing the new extensometer, and the re-designed chronograph. A single glance at the former was enough to show its great superiority to the older instruments. The method of keeping the silk cord in tension by means of two opposing weights, and the method of bringing the mirror back to the scale, both struck him as being especially ingenious. While the idea of water-cooling the connecting pin was very good, in that it disarmed criticism, his experience was that it was absolutely unnecessary, an experience which was also borne out by Mr. Ewen in his paper on antimony-lead alloys.

Fig. 5 showed the characteristic expansion-crystallization-interval diagram, the two curves presenting a striking general similarity but considerable local divergencies. The similarity seemed to be rendered the more puzzling by the theory set forth in the second part of the paper,

that the expansions were due to different causes in different alloys. Indeed, the paper, while clearing up many points, only served to indicate once again the tremendous complexity of the whole subject.

Part II. of the paper he (Mr. Haughton) considered especially valuable, particularly that section dealing with the heating of the bars, which seemed definitely to prove that, in many cases at any rate, the expansion during solidification was not due to crystal thrust.   With reference to the 90 per cent. copper-tin alloy, Mr. Chamberlain suggested " that the expansions produced are due in some way to the effect of the cold mould chilling the liquid solution between the dendrites of the solid solution *a*," but he (Mr. Haughton) did not find it easy to understand how that chilling caused an expansion.   On the other hand the explanation of the volume change in aluminium seemed to be particularly satisfactory, and in all similar cases where dissolved gas was the only factor, or the chief factor, producing expansion, it was easy to understand the agreement between the curves of expansion and crystallization interval.

Mr. CHAMBERLAIN wrote, in reply to Mr. Haughton's communication, that he would like to point out that although in the second part of the paper it was indicated that expansions were due to different causes in different alloys, there was no suggestion that the expansions observed in the copper-aluminium series were not all of one kind ; further work on the melting of bars of copper-aluminium alloys was necessary before that could be proved, and the author had in view further experiments in that direction.   At present the actual observations of the fractured castings in the copper-aluminium series (p. 202), and the experiments on the melting of pure aluminium bars, rather pointed to expansions in this series of alloys being produced by the same cause, namely dissolved gases in the alloy.

The author was fully aware that it was difficult to understand how the chilling effect on the copper tin alloy caused the expansion ; the fact remained that a bar of the metal slowly cooled from the liquid state showed no expansion, and on once annealing a casting of this alloy the phenomenon of a contraction or an arrest on melting the bars disappeared. This fact led the author to make the suggestion that in the copper-tin alloys the expansion observed was due to a chilling effect.

ON THE COPPER-RICH KALCHOIDS *

(COPPER-TIN-ZINC ALLOYS).

By Professor SAMUEL L. HOYT (University of Minnesota, U.S.A.).

INTRODUCTION.

THE plan of the present research was formulated at Columbia University upon the suggestion of Dr. Campbell, director of the metallographical laboratory, and is intended to fulfil part requirements for the Ph.D. degree in that university. After the completion of the preliminary work at Columbia University, the research was transferred to the metallographical department of the " Eisenhüttenmännischen Instituts " at the Royal School of Technology, Charlottenburg, under the direction of Dr. Hanemann.

The constitution of the ternary alloys of copper, tin, and zinc up to about 50 per cent. zinc and 30 per cent. tin, has been studied both by thermal and micrographical analysis. The term " kalchoid " has been chosen to designate the ternary alloys of copper, tin and zinc, as was first suggested by Thurston. This saves such names as brass and bronze for their more correct application and avoids confusion.

REVIEW OF LITERATURE.

The author will now turn to a brief consideration of the more important literature dealing not only with the kalchoids but with the two component systems copper-zinc, and copper-tin as well.

ON THE COPPER-ZINC SYSTEM.

The first work of importance on the constitution of the brasses was published in 1896 by Charpy,† who studied the microstructure and mechanical properties of the commercial alloys up to about 50 per cent. zinc. He noticed

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* Read at Annual Autumn Meeting, Ghent, August 29, 1913.
† Charpy, *Bulletin de la Société d'Encouragement*, I., 1896, p.180.

the peculiar behaviour of the β constituent in the 35 to 45 per cent. alloys and was inclined to consider this constituent amorphous, although he failed to recognize it under the guise of the coarsely crystalline alloys of 48 per cent. zinc.

In the following year, Roberts-Austen published the first complete freezing-point curve, along with the peritectic horizontals and a further line $e'' \, e'$ called by him "eutectic." * The presence of this eutectic was immediately contested, Charpy in a second paper † pointing to the fact that the ground mass, while undoubtedly fine-grained, still failed to exhibit the characteristic structure to be expected, as in the case of the steels.

In 1904 Shepherd published the first complete constitution diagram, which is too well known to require especial discussion. He failed to find the line $e'' \, e'$ of Roberts-Austen either pyrometrically or micrographically, and ascribed it to experimental error. Shepherd in discussing the solid solutions, refused to regard the composition with 60 per cent. zinc as a compound, Cu_2Zn_3, as is to be inferred however from the diagram. This phase is of great importance in the ternary alloys, and its behaviour, as both solid solution and chemical compound, is not without significance.

In 1906 Guillet ‡ published some work on the brasses in connection with his investigation of the influence of the addition of tin to the brasses. This agrees with Shepherd's work and will be considered further on under the literature on the ternary alloys.

Then two other works appeared, both bringing additional evidence to support Shepherd in his diagram. Bengough and Hudson § in their experiments on the heat treatment of Muntz metal, and Tafel ‖ in his determination of the copper-zinc diagram, advanced microscopical and thermal evidence indicating that Roberts-Austen's line $e'' \, e'$ was an error.

* Roberts-Austen, *Fourth Report Alloys Research Committee*, 1897.

† Charpy, *Bulletin de la Société d'Encouragement*, II., 1897, p. 414.

‡ Guillet, *Revue de Métallurgie*, iii., 1906, p. 243.

§ Bengough and Hudson, *Journal of the Society of Chemical Industries*, xxvii., 1908, pp. 43, 654.

‖ Tafel, *Métallurgie*, v., 1908, p. 343.

In a paper by Carpenter and Edwards * presented to the Institute of Metals in 1911, the line e'' e' was again brought up. The authors (Carpenter and Edwards) sought to re-establish this line in the diagram chiefly by a series of very accurate curves covering the β range and supported by photomicrographs. They drew attention to certain peculiarities in the alloys of this range which were readily explained on the assumption that such a line existed. In the author's opinion, the curves were very satisfactory evidence, but he will attempt to show later that the photomicrograph given can hardly be accepted as exhibiting a duplex structure, as was stated in the above-mentioned paper.

To meet the criticism which this first paper called forth, Carpenter presented a second paper,† in which he described further experiments to prove the $\beta \rightleftarrows \alpha + \gamma$ inversion. He discussed annealing experiments on two different compositions near the eutectoid point, the one containing a slight excess of α, the other a slight excess of γ. After several weeks of annealing at $445°$ C., a typical duplex structure was obtained, leaving no doubt as to the existence of the line e'' e' of Roberts-Austen.

In two more recent papers, Carpenter ‡ reported further work on the $\beta \rightleftarrows \alpha + \gamma$ inversion, dealing with the resolution of free β and the effect on this breakdown of the addition of third metals. In the first of these two papers, he gives a very interesting cooling curve showing rather conclusively that α and γ do not reunite at some lower temperature to form perhaps a chemical compound, copper-zinc.

A study of the electrical conductivity of the brasses has been of great interest. In the α field the results check very closely with the thermal and micrographical analyses, but as soon as the β field is entered we find a big discrepancy. The curve, instead of running linear from 37 per cent. zinc to 60 per cent. zinc, as would be expected from the diagram, runs linear to a maximum at about 49 per cent. zinc and again linear to about 59 per cent. zinc. From this it would seem that apparent β behaved under these conditions as a

* Carpenter and Edwards, *Journal of the Institute of Metals*, No. 1, 1911, vol. v.

† Carpenter, *Journal of the Institute of Metals*, No. 1, 1912, vol. vii.

‡ *Ibid.*, No. 2, 1912, vol. viii.

homogeneous solid solution.   As above mentioned, a cooling curve shows that α and γ evidently do not reunite; thus we have the paradox that β, though known to be heterogeneous, behaves as a homogeneous solid solution.   This point awaits yet a satisfactory explanation.*

Potential measurements as well as chemical behaviour have been used to study the constitution of the brasses,† but little additional of a definite nature has been learned.

On the Copper-Tin System.

The part of the copper-tin diagram important to this research appeared long since, being substantially that given by Heycock and Neville in 1903.‡

Two other investigations followed, by Shepherd in 1906 § and Giolitti in 1909.‖

The important points for the present paper are the limit of saturation of the α solid solution, the temperature of the eutectoid inversion, and the composition of the eutectoid point. The limit of saturation varies from 5 per cent. in Giolitti's diagram to 13 per cent. in Shepherd's; while the eutectoid point remains more constant at approximately 26 per cent. Its inversion temperature is given from $486°$ to $500°$ C.

In a very careful cooling curve taken by Heyn and Bauer ¶ on an alloy containing 83.5 per cent. copper, 16.0 per cent. tin, 0.2 per cent. zinc, with small amounts of arsenic and lead, this temperature is given as $525°$ C.   (See Fig. 1.)   This curve was recorded by taking the time Δt required for the alloy to cool, an interval of $10°$ C. Measurement of the electrical potential has been used by

* See Guertler, *Zeitschrift für anorganische Chemie*, 51, 1906, p. 397, and Luigi Norsa, *Comptes Rendus*, 155, p. 348, 1912.

† See for reference on "potential measurements," Laurie, *Journal of the Chemical Society*, 53, 1888, p. 104 ; Herskowitch, *Zeitschrift für physikalische Chemie*, 27, 1898, p. 123 ; Puschin, *Zeitschrift für anorganische Chemie*, 56, 1907, p. 1. For "chemical behaviour" : Lincoln, Klein, and Howe, *Journal of Physical Chemistry*, xi., 1907, p. 501 ; Sackur, *Arb. k. Gesundheitsamt*, xx., 1904, p. 512, and xxii., p. 127.

‡ Heycock and Neville, *Philosophical Transactions*, 202, 1903-4, p. 1.

§ Shepherd and Blough, *Journal physikalische Chemie*, x., 1906, p. 515.

‖ Giolitti and Tavanti, *Gazetta Chimie*, 38, 1908, p. 209.

¶ Heyn and Bauer, *Mitteilungen an den Königlichen Materialprüfungsamt*, xxix., 1911, p. 29.

Laurie,* Sackur and Pick,† Puschin,‡ and Ledoux § to study the composition of the bronzes. This work has shown that the constituent δ is a solid solution, and not the compound
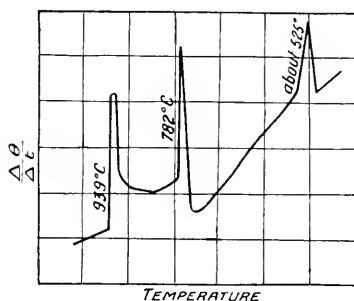
FIG. 1.—Heyn and Bauer. Cooling curve of alloy : Copper, 83·5 per cent. ; Tin, 16·0 per cent. ; Zinc, 0·2 per cent.

Cu_4Sn; further the existence of the compound Cu_3Sn was established. These results were also confirmed by Guertler's work on the electrical conductivity of metallic alloys.‖

ON THE COPPER-TIN-ZINC SYSTEM.

Except for the work of Thurston ¶ on the mechanical properties of the kalchoids, there has been no systematic research covering the entire range of the commercially important copper-rich ternary alloys. There has, however, been considerable work done in single branches on physical and chemical measurements, and the influence of tin on the mechanical properties and microstructure of the brasses. Although the work of Thurston offers considerable matter of a speculative nature on the constitution of the kalchoids, still, since it deals mainly with the mechanical properties, it (and other similar work) will not be considered here.

Guillet ** in 1906 published a series of experiments on the

* Laurie, *Journal of the Chemical Society*, 53, 1888, p. 104.
† Sackur and Pick, *Zeitschrift für anorganische Chemie*, 58, 1908, p. 46.
‡ Puschin, *Zeitschrift für anorganische Chemie*, 56, 1907, p. 1.
§ Ledoux, *Comptes Rendus*, 155, 1912, p. 35.
‖ Guertler, *Zeitschrift für anorganische Chemie*, 51, 1906, p. 397.
¶ Thurston, *Materials of Engineering*, vol. iii.
** Guillet, *Revue de Métallurgie*, iii., 1906, p. 243.

mechanical properties and the microstructure of the kalchoids up to about 10 per cent. tin. It is interesting to note that in his photomicrographs evidence pointing to the eutectoid inversion is given in the appearance of the eutectoid structure upon the addition of about 3 per cent. tin to the 30 per cent. brass, which point, however, seemed to escape his notice. But the presence of a " constituant spécial " in the microstructure of the alloys with more tin did attract his attention. This " special constituent " was observed if tin was added directly to $a + \beta$, when the tin content exceeded a certain amount, depending on the zinc content.

On adding tin to $a + \beta$, the tin was considered first to enter the a up to 0·7 per cent. tin, and then to enter the β. Any excess formed the " special constituent." (This special constituent observed by Guillet will be seen later—under the discussion of the microstructure—to be the γ solid solution; and the irregularities he notes in this field will be seen to be due to the influence of tin on the eutectoid inversion.) It was in this field, just off the $a + \beta$ range, that a remarkable improvement in the properties was noticed. This, Guillet attributed as due to the " special constituent," which conclusion, the author believes, should not necessarily follow. The author holds rather to the opinion that the rapid rise in properties is due to the tin going into " apparent " solution, without forming the special constituent.

Miller,[*] in a series of experiments testing the influence of various metallic and non-metallic elements on the properties of normal statuary bronze, determined the melting points of ten copper-rich kalchoids, which were used for comparison in the construction of the ternary diagram. Nothing of their microstructure was noted by him, as the constitution of these ternary alloys was at that time not understood.

Johnson,[†] in a paper before the Institute of Metals, discussed the influence of tin on the microstructure of the brasses. He seemed inclined to discredit the theories advanced by Guillet, in that he considered the eutectoid structure due to the formation of a compound Cu_4Sn, which gave the cus-

[*] Miller, *Metallurgie*, ix., 1912, p. 63.
[†] Johnson, *Journal of the Institute of Metals*, No. 1, 1912, vol. vii.

tomary eutectoid of the copper-tin series. Considerable stress was laid on the importance of the influence of tin on brass, but nothing conclusive could be offered at that time.

As mentioned above, Carpenter read a paper on the effect produced by the addition of third metals to the pure structurally free β. In this the influence of tin was discussed, with the conclusion that 0.995 per cent. tin caused the resolution, so that it was visible under 150 diameters,—an accompanying photomicrograph * being cited as evidence. It will be seen later that the case is hardly so simple as it appears from this paper; and indeed, in the author's opinion, Professor Carpenter's photomicrograph does not show the eutectoid structure. If the eutectoid structure is present, it can be and should be, the author believes, clearly and undeniably shown. . . .

Photomicrographs 16, 17, and 18 on Plate IX. of the present paper show the desirability of correlating high and low magnifications for the sake of illustrating such a point.

EXPERIMENTAL WORK.

The metals used for this research were electrolytic copper, practically pure, and Kahlbaum's best grades of tin and zinc. The melts were made up to weigh approximately 50 or 100 grammes, the latter in case the cooling curve was to be taken. For preparing the alloys, two furnaces were used. That employed in case the melts were to be cast (chill cast in an iron mould), was constructed in the laboratory : a small gas-fired furnace with blast, in which a temperature of 1200° C. could be easily maintained. The other, a large natural-draught gas furnace—giving fairly good insulation but at the same time handy to work with—was used in case cooling curves were to be taken. Special attention was paid to keeping the temperature carefully regulated, especially in preparing the 100 gramme alloys. No uncommon |difficulties arose, both furnaces working satisfactorily. Hessian crucibles were used. As a guard against oxidation, a cover of borax (or of finely ground coal, which was used in the large furnace) gave very good results—the one disadvantage of the borax cover being that the borax attacked the walls of the crucible and also

* *Journal of the Institute of Metals*, No. 2, 1912, vol. viii. Plate xvi. 7.

took up copper from the melt. The 50 gramme melts, after preparation, were either allowed to cool in the furnace, or, in order to produce a fine-grained structure, were chill cast in a small iron mould ; while in the case of the 100 gramme alloys, the thermal element was inserted in the melt and its cooling curve taken direct.

It was considered necessary to analyse the 50 gramme alloys, and throughout, the following method was employed. First the tin was removed by dissolving 1 gramme of the alloy in concentrated nitric acid, and filtering the tin off as metastannic acid. The copper in the filtrate was determined by the iodine and thiosulphate method described in the *Journal of the American Chemical Society* for December 1911. In this method the nitric acid is destroyed by sodium hypochlorite. The following solutions were used : (1) Sodium hypochlorite, made by boiling 112 grammes calcium hypochlorite with 100 grammes anhydrous sodium carbonate in 1200 cubic centimetres water and filtering ; (2) a 5 per cent. solution of phenol ; (3) sodium hydrate 20 per cent. ; (4) acetic acid 50 per cent. ; (5) potassium iodide 30 grammes per 100 cubic centimetres ; (6) sodium thiosulphate for titration ; (7) starch indicator. The determination was carried on in this order : (1) pipette off 50 centimetres of the filtrate (made up to 250 cubic centimetres) into a 300 cubic centimetre Erlenmeyer flask, and add from 2 to 4 cubic centimetres of the hypochlorite (or until the green colour appears and chlorine gas is given off) ; (2) add 10 cubic centimetres phenol to take up the chlorine, blowing out any remaining ; (3) add sodium hydrate until a slight precipitate forms (add immediately otherwise nitrophenol forms) ; (4) add acetic acid till precipitate disappears ; (5) titrate for copper with sodium thiosulphate, as usual. The zinc is taken as the difference.

To determine the composition of the 100-gramme alloys used for the cooling curves, the method of weighing before and after preparation was employed. Loss in weight was attributed to zinc volatilization ; but whenever excessive loss in weight, inhomogeneity, or the like, gave rise to any doubt, the melt was laid aside and not used.

Certain of the alloys were subjected to annealing, which was

usually carried on in an ordinary Heraeus furnace, the specimens being sealed in an iron pipe to prevent oxidation. The time of annealing averaged about forty-eight hours, the current being taken from a storage battery for overnight work. For etching, two reagents were used, basic cuprous chloride and acid ferric chloride. These reagents work in like manner, attacking the copper-rich constituent first and leaving the γ a bright grey. The basic cuprous chloride is preferable for the zinc-rich alloys, the acid ferric chloride for the tin-rich.

In making the thermal analysis (1), the $\frac{\Delta t}{\Delta \Theta}$ method was employed when a complete cooling curve was taken ; (2) the $\frac{\Delta(\Theta - \Theta')}{\Delta \Theta}$ method, when transformations in the solid state were to be definitely located. Under the first method, intervals in time were recorded by a Richardson chronograph. After considerable unsatisfactory experimenting with the platinum element, other elements were tried, and finally one of nickel wire and constantin wire of 6 millimetres diameter was found to be most suitable, and was employed in all subsequent work. This element remains exceptionally constant under varying conditions, and has a very high thermo-electric force such that with a resistance of 1200 ohms (including the resistance of the galvanometer) 1 millivolt is equal to only about $33°$ C. On continued heating, the nickel wire becomes brittle and the element must be frequently replaced ; however, this counts as a very small item against it, when we take into consideration its cheapness. The compensation element was made of two pieces of constantin wire connected by a 5 centimetre piece of nickel wire. Electrolytic copper was used as the neutral body. All work was done in an atmosphere of illuminating gas.

The copper-zinc alloys were made for the purpose of studying their microstructure, the β structural constituent in particular. Unaware that Professor Carpenter was already working out the eutectoid inversion, the author had started a special research to test the alloys in this range for the $\beta \rightleftarrows a + \gamma$ inversion, when Professor Carpenter's work came to hand. Further research in this particular line was then given up (and willingly given up, it might be confessed, for, as is well known, this breakdown, though unmistakable in the thermal analysis, can

be proven micrographically only with extreme difficulty!).
The copper-tin alloys were made up for the purpose of ex-
amining their microstructure, locating the limit of saturation
of the α solid solution, and studying the eutectoid inversion of
the β solid solution.   The limit of the α solid solution was
taken at 10 per cent., and the eutectoid temperature as
$525°$ C.

The ternary alloys were chosen in order to study the con-
stitution of those copper-rich alloys within the commercial
range.   Although the diagram, Fig. 6, has been drawn com-
plete, the dotted lines are to be regarded as constructed on
purely theoretical grounds.   The liquidus surface consists of
two parts (that is, up to 30 per cent. tin and 50 per cent. zinc)
corresponding to the equilibria α + liquid and β + liquid.
The line between the α and β surfaces was determined by
noting at what compositions the peritectic point disappeared;
but this same line for the β and γ surfaces is purely theo-
retical.   That the α surface extends far out into the diagram
—considerably farther than one might expect—is from the
thermal evidence unmistakable.   The temperatures of the
liquidus surfaces are shown by the contour lines.   The solidus
surfaces run under the liquidus surfaces in the same manner
in which the solidus lines follow their co-ordinate liquidi in
the two binary systems.   We have two surfaces which corre-
spond to the separation of the α and β solid solutions from
their melts, viz., the planes 1–4–4 and 5–5–10–10 in Fig. 3.
These surfaces are connected by the peritectic surface 4–4–2–2.
The line 5–5, called " maximum peritectic," was drawn to show
about where the corresponding points in the binary systems
would come in the ternary diagram.   On the copper side of
this line, the alloy going solid with the peritectic reaction α +
liquid $\rightleftarrows$ β, the cooling curves show a sharp return from 'the
peritectic maximum; while on the other side, as the alloy
still remains part liquid (β + liquid), the cooling curves exhibit
a much slower return, corresponding to the freezing of the re-
maining liquid.   The other part of the peritectic surface ex-
tends up to the line 2–2.   A second peritectic surface runs
from 10–10 to 3–3, at which temperature β reacts with the
melt.   This is clearly to be seen on the cooling curves.   The

evidence is not sufficient to locate these lines absolutely.
Between the lines 5–5 and 10–10, the alloys solidify as a
series of solid solutions, according to the reaction β + liquid
$\leftrightarrows \beta$ – to be seen on examining the cooling curves.

Since we find no fundamental difference in the behaviour
of the ternary alloys, on solidifying, from that of the binary
alloys, the ternary alloys may be termed "pseudo-binary."
Following the lines through the system as indicated, the
process of solidification of any alloy may be seen at a glance
and at the same time compared to that of any corresponding
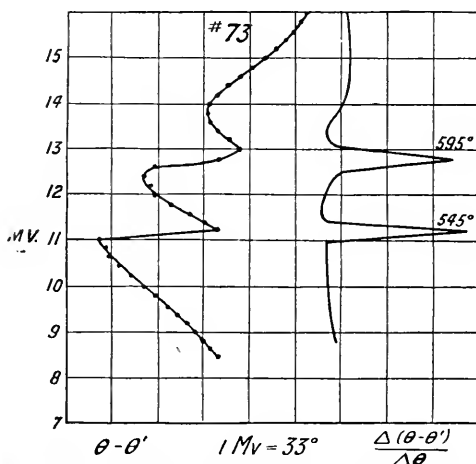
FIG. 2.—Alloy 73.   Heating Curve and 1st Derivative: Copper, 75 per cent.;
Tin, 15 per cent.; Zinc, 10 per cent.

alloy, or, better expressed, group of alloys of either the copper-
tin or copper-zinc series (see Figs. 3 and 4). For example,
the ternary alloys within the area 1–4–4 solidify just as
do the binary alloys from 1–4; furthermore, the alloys of
the field 4–4–8–8, as those from 4–8; of the field 4–5–
5–4, as those from 4–5, &c. (In this scheme it is to
be noticed that the corresponding points have in all cases
the same numbers.) To determine the composition of the
solid phase separating from the liquid, it is necessary to pass
a horizontal plane (temperature) through the point in ques-
tion on the liquidus surface, noting its intersection with the

corresponding solidus surface. Now this temperature plane
intersects the two surfaces in a line, so that we have two
lines 2′–2′ and 4′–4′ running from the copper-tin system to
the copper-zinc system, as shown for the two surfaces 1–4–4
and 1–2–2 in Fig. 3. Along the lines 2′–2′ and 4′–4′,
there will be pairs of concentrations in equilibrium with each
other, as represented by the end-points of the parallel lines.
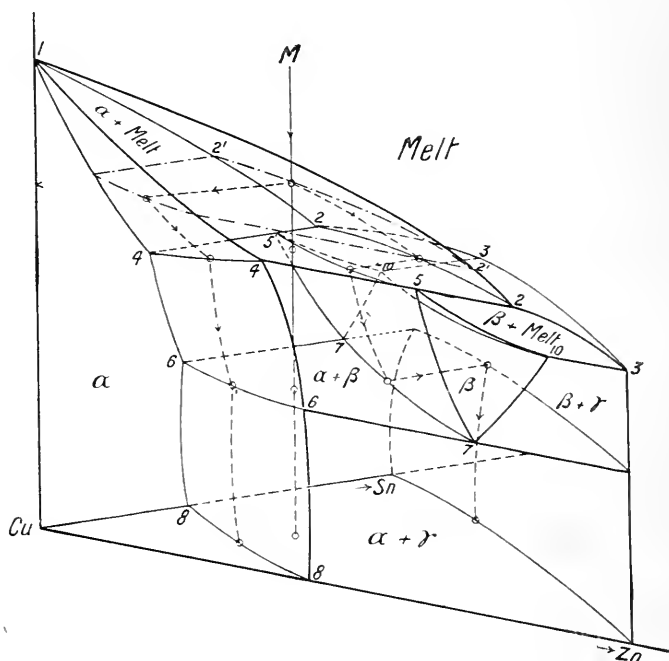
FIG. 3.—Scheme for the Copper-Tin-Zinc Ternary Diagram.

These lines, of course, are drawn in empirically, and are
intended to show merely qualitatively the relation between
the liquid and the solid in equilibrium.

For each temperature, such a plane, with co-ordinate points
in the liquidus and solidus surfaces, could be constructed; and
by means of such a diagram, the complete solidification of the
alloy could be traced, and the composition of the phases at
each temperature, and the relative amounts of each phase

corresponding, be determined. The relative amounts are to each other inversely as the distance of the phasial compositions from the characteristic line of the alloy, " characteristic line of the alloy " meaning the vertical corresponding to the total composition of the alloy. This method of determination may be applied in other fields of the diagram also. Thus far, in solidifying, the ternary alloys have behaved as simple
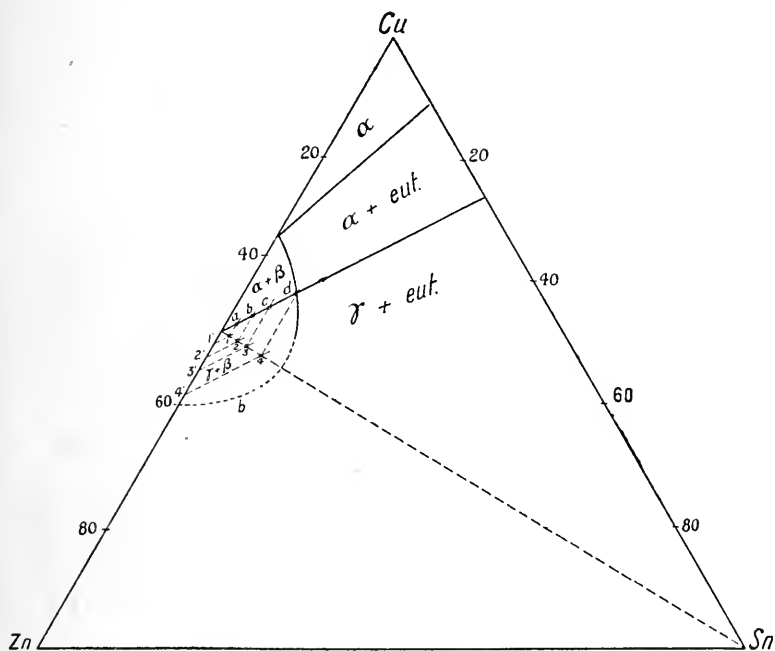
FIG. 4.—The line *ab* is plotted for Alloys cooled in the Furnace.

solid solutions of tin + zinc in copper—that is, as pseudo-binary alloys with copper as the solvent; moreover, except for what might at first seem to be irregularities due to the relative qualitative effect of the tin and zinc,* the kalchoids apparently undergo their transformations in the solid state analogously to the binary alloys, this with a single exception to be taken up later in the work.

* The appearance of the eutectoid structure in alloys of 1·5 per cent. tin, for instance, or the special constituent noted by Guillet, and referred to on p. 240.

The field 4–8–8–4 gives the variation of saturated α with temperature, the alloys in the field 1–8–8 at normal temperatures being simple homogeneous solid solutions. The surface 5–5 to 7–7, the conjugate surface to the surface 4–4–6–6, gives the variation of saturated β with temperature toward the copper corner. The line 7–7 connects the various eutectoid compositions from 26 per cent. tin to 48 per cent. zinc. The scheme discussed already may be used here in following the behaviour of α and β on cooling. The concentration of α varies along the surface 4–4–8–8, while that of β varies along the surface 5–5–7–7. Disregarding for the moment complications in the pure copper-tin alloys, which doubtless extend some distance into the ternary diagram, on the γ side of the eutectoid line, the solid solutions γ and β are in equilibrium. The β solution follows the surface 10–10–7–7, the γ remaining fairly constant in composition on a nearly vertical plane through the " γ line." Between these two regions, there is a region of pure β formed either by the peritectic reaction in the field 2–2–5–5 or from the liquid directly in the field 2–10–10–2. This field narrows down with a drop in temperature from the lines 5–5 and 10–10 to the eutectoid line 7. With this in mind, it is easy to see how the alloys in this region of pure β behave on cooling. In the solid bounded by surfaces 4–4–8–8 and a plane through the line 5–5, the alloys solidify as $\alpha + \beta$. In the little region bounded by the surface 4–4–8–8 and a vertical plane through 4–4, the β goes into solution on cooling. In the remainder of the solid, α and β vary in composition on cooling, as given, until at the eutectoid point, the solution breaks up, giving the $\alpha + \gamma$ complex. In the solid 5–5–7–7–10–10 corresponding to pure β, the alloys separate out primary α on one side of the eutectoid line and primary γ on the other side. Along the line 7–7, of course, there is no primary segregation, the alloy going over into a simple eutectoid. As regards the β-phase and its behaviour in this series : in the pure copper-zinc system, β being one phase, and containing two components, has two degrees of freedom. At the breakdown $\beta \rightleftarrows \alpha + \gamma$ (there being now three phases), the system becomes non-variant, and so the change

occurs with the temperature remaining constant. In the present case, however, there are three components, the number of phases remaining the same; that is to say, the system now has one degree of freedom at the moment of inversion. As the simplest case of this, we could have a breakdown corresponding to that found by Carpenter and Edwards in the copper-aluminium-zinc alloys, running from the one eutectoid point directly to the other, the temperature varying between the two end temperatures as a linear function of the composition; in which case one of the degrees of freedom is suppressed. Or the breakdown might just as well occur in a manner analogous to a series of solid solutions separating out of their melts, which series may run linear or have a maximum or a minimum. In this system a maximum is obtained near the middle point of the eutectoid line, as is seen from the section through the diagram along this line.

Another point of importance is the eutectoid structure. As is well known, the β constituent appears homogeneous under the microscope, but long annealing produces its true duplex structure. This is due to the fact that though the " apparent β" is composed of minute α and γ particles, still these particles are so extremely fine, ultramicroscopic, that it is impossible to distinguish them. It is interesting to note what influence the addition of tin exerts:—Do the α and γ particles, their compositions thus changed, become enabled to coalesce into larger grains, thereby rendering themselves visible under the microscope ? This problem has been discussed by Professor Carpenter,* who added tin in varying amounts to the pure apparent β constituent of the brasses, 48 per cent. zinc. This is shown diagrammatically in Fig. 4, in which the alloys, having the desired tin content, are plotted by the points 1, 2, 3, and 4. By drawing lines parallel to the eutectoid line, we obtain the approximate composition of the pure copper-zinc alloys having a corresponding microstructure.† The γ segregate shown in Professor Carpenter's photomicrographs is therefore easily explained, and should not, on examination under

* *Journal of the Institute of Metals*, No. 2, 1912, vol. viii.

† In a criticism of Professor Carpenter's paper, Professor Huntington has called attention to this fact.

a low power, be mistaken for a eutectoid structure. In a discussion of the microstructure for the purpose of studying the effect of tin addition on the apparent homogeneous structure of the β constituent, it would be more proper to choose the compositions indicated by the points a, b, c, which lie on the eutectoid line and contain the amounts of tin to be investigated. If in this manner a certain point can be located, beyond which the eutectoid structure is readily apparent, then it may be said that the percentage of tin added caused the visible breakdown of the β constituent. In reality, this appearance does not confine itself to the eutectoid line, but may be followed over a field shown by the line 1-2, as may clearly be seen from an examination of the microstructure. But while the excess of γ on the one side (or the excess of a on the other) undoubtedly plays an important role in absorbing crystals of its own kind out of the ground mass, still the actual chemical composition and the rate of cooling seem to be the all-determining factors. In certain alloys (12) of the pure copper-zinc (55 per cent. zinc) series and (45) of the ternary series, we have about the same relative proportions of segregate and ground mass; but while the former alloys would probably require severe annealing just below the transformation point, the latter yields the eutectoid on normal cooling.

Now to get an idea of the influence of time on the breakdown, having considered that of the chemical composition, the author compared chill-cast specimens, slowly cooled specimens, and annealed specimens. By plotting lines such as in Fig. 4, to show the limiting compositions of the apparent β structure, it was seen that this field contracts toward the copper-zinc side as the time of cooling is increased. Two examples of this may be cited : alloy No. 6 (copper, 57·4 per cent. ; tin, 11·2 per cent. ; zinc, 31·4 per cent.) is shown as chill cast, Plate IX., Fig. 19 ; and again, Plate IX., Fig. 20, after being annealed 48 hours at 450° C. In Plate IX., Fig. 19, we have the γ segregate in a ground mass of apparent β, which, on examination of Plate IX., Fig. 20, is seen to have been converted into $a + \gamma$. This conversion is evident from the increase in the relative amount of γ, and is also recognised

on microscopical examination, when the solid solutions a and β may usually be distinguished.

The behaviour of alloy 54, which was cooled slowly in the furnace, was also very interesting. Superficially, this alloy consisted of the γ segregate in a ground mass of apparent β, but on examination under a higher magnification, it was found to be quite otherwise. Fig. 24, Plate X., shows the interior of a crystal and is seen to be, as above suggested, γ segregate $+$ apparent β. If we examine the edge of this crystal, we see that β is breaking down with the formation of the $a + \gamma$ eutectoid. This may be seen on referring to Plate X., Figs. 25 and 26. In Fig. 25, in certain localities, there appears a parallelism in structure. This is the $a + \gamma$ eutectoid, shown at better advantage in Fig. 26. This is seen very clearly under the microscope, but such a clear effect cannot be reproduced in photograph because of the haziness of the structure itself, and because of the nearly equal effect the colours of the various phases have on the photographic plate.* Fig. 26 shows an area of well-formed and unmistakable eutectoid structure, lamellar the same as on the a side. From this it seems quite evident that considerable inertia must be overcome in order to bring about a visible resolution of β. The effect will be to lower the inversion temperature by supercooling, as well as to diffuse it over an interval of temperature, at times obliterating it altogether.

The fact that an appreciable amount of tin may be added to certain brasses without causing any noteworthy change of structure, is of decided practical importance. For a fuller appreciation of this fact, let us compare the structure of alloys in which tin is in apparent solution with that of those in which there is a visible breakdown. Take, for example: (1) an alloy in the group called by Thurston the " maximum kalchoids "—that is, an alloy in the little field in which the tin goes into apparent solution (there the structure corresponds to that of the pure β constituent); (2) an alloy, for example No. 68 (see photomicrographs 11 and 12, Plate VIII.), in which we have the eutectoid structure. That is to say, in the first

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* The author suggests that Fig. 25 be examined under a hand-glass—then the eutectoid is very evident.

alloy, the advantage of adding tin is fully realized, the alloy being able to retain the desirable structure; while in the second, the eutectoid structure is produced, the mechanical properties dropping in value to practically nil. The importance of locating the limits of this field is self-evident. Thurston has shown the rapid depreciation of the mechanical properties in this field upon the continued addition of tin to be much more rapid than is to be explained on the ground of the simple increase of tin content. Thus the tensile strength rises very rapidly from $50,000$ to $65,000$, then decreases sharply to 5000 on crossing a relatively small area in composition.

The diagram shown in Fig. 5, and again on a larger scale in Fig. 6, was constructed on thermal and micrographical evidence, using the scheme suggested by the perspective in Fig. 3 as a guide. At the present writing, the author is not prepared to submit the entire evidence on the eutectoid inversion, for the reason that certain irregularities are yet unsolved; if possible, it will be given complete later in an appendix. Little need be said concerning the determination of the liquidus and solidus surfaces. The two binary diagrams of Shepherd were used as a basis for constructing the liquidus surface, the corresponding temperatures being projected on to the ternary triangle. Then the direction of each contour was determined by plotting the melting points obtained in the research. Allowing for experimental error, these lines run uniformly through the field. The changes in direction which the contours take on crossing 2–2, though not pronounced, can always be clearly seen; and this method of locating line 2–2 checked nicely with the other more accurate method (*i.e.* that of locating the line by using the peritectic transformation point) which was employed. Miller's determinations were plotted but found to be too irregular for use here. The solidus surfaces, as determined from the cooling curves, are seen to run underneath the liquidus surfaces as indicated in Fig. 3. The surface 1–4–4 was not determined. The surface 4–4–2–2 was found to run irregularly from the one binary series to the other; upon the addition of tin, dropping rather rapidly from the copper-zinc side until it ran nearly horizontal
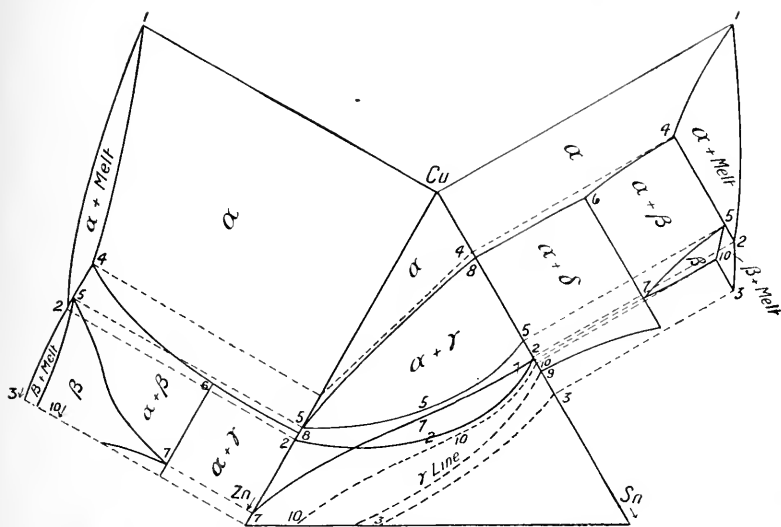
FIG. 5.—The Copper-Tin-Zinc Ternary Diagram.
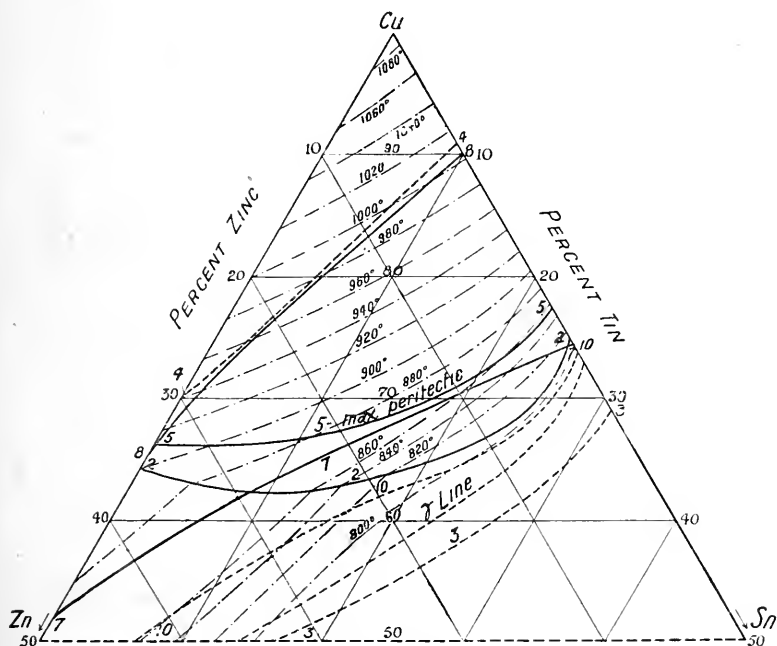
FIG. 6.—The Copper-Tin-Zinc Ternary Diagram.

to the copper-tin side.   Between lines 5–5 and 2–2 the sur-
face drops until it reaches line 2–2.   From line 2–2 to line
10–10, the alloys solidify over a small interval of temperature,
giving the β solid solutions.   The line 10–10 was located by
observing at what compositions the second peritectic reaction
(β + liquid $\leftrightarrows \gamma$) entered.   Of great importance is the location
of the transformations in the solid state, especially the eutectoid
inversion.

Considering first a section through the diagram along the
eutectoid line 7–7 [see Appendix], we see, as stated above,
that instead of running linear from copper-zinc to copper-tin,
it rises to a maximum near the middle, corresponding to
590° C. (using the mean of the temperatures on heating and
cooling).   This inversion point, as obtained from the cooling
curve taken direct from the liquid, is subject to super-cooling.
The most noticeable effect of super-cooling occurs in the alloys
with small per cent. tin just off the copper-zinc diagram ; here
the inversion point is either so weak or so diffused as to be
scarcely recognizable.   That this should be so is a natural con-
clusion from the discussion of the influence of tin on the
inversion.   Beyond 10 per cent. tin the point is clear and
well defined, but still subject to a super-cooling of from 15°
to 30°—taking the maximum difference between the point on
heating and the (same) point on cooling.   When the maximum
is passed, the inversion drops off regularly toward the copper-
zinc series.   To obtain the inversion temperatures more
accurately, and especially on the zinc side, curves were taken
by the compensation method.   On plotting the points this
time, the maximum was again seen clearly, and a rise in the
individual temperatures was observed.   It was interesting to
note how the addition of only 1 per cent. tin was sufficient
to raise the inversion temperature of β brass from 477° to
495° C., a good example of the enormous influence which the
addition of even quite small proportions of a third element
may exert.*

Another point under consideration was whether the heat

* To the author's mind, this case would serve to illustrate why it is preferable to
consider such a system ternary, rather than, as is customary, regard it as a binary
system with a third metal added.

effect took place at a constant temperature or over an interval of temperature, forming in this way a major and a minor curve intersecting at the maximum. The determination of this point—a thing possible enough theoretically—is made considerably more difficult by the fact that the heat effect is diffused over an interval, through the inherent nature of the reaction. It can be said with certainty that the inversion does occur at constant temperature at the maximum, and that on either side it has the appearance of being an interval.

The temperature of the eutectoid point is raised with increase in the copper content also, so that the effect on the inversion temperature of the brasses produced by the addition of tin, is in turn remarkably increased with the increase of copper. On crossing the line 2–2, when above the eutectoid section 7–7, this rise in temperature is very rapid— which fact leads to speculation as to why this happens. The 3 tin, 29 zinc alloy, for example, shows an inversion temperature of $570°$ C. as compared to $480°$ in an alloy of 6 tin and 33.5 zinc, which is just below the line. From this evidence, one might be led to suspect the existence of an additional line in the diagram ; but outside of this there was no reason at all for considering the change in temperature to be other than a linear function of the composition.

The greatest deviation was noticed in the field between the lines 7–7 and 8–8 on the tin side of the maximum. Much to the author's astonishment, two well-defined heat-effects were recorded on every alloy tested in this region both on the first or direct curve and on the compensation curve. For example, see Fig. 2, which is the heating curve of an alloy with 15 per cent. tin and 10 per cent. zinc with its first derivative. The effect is noticeable up to the eutectoid line but does not cross it on the decrease of copper. Being unable just now to report fully on this appearance, the author wishes to leave it an open question, until it has been more completely worked out ; then this, and likewise the eutectoid inversion over the entire range, which bears close relation to it, will be discussed in detail. The micro-

structure of this alloy will be considered briefly further on.
The eutectoid inversion on the tin-zinc side of the line 7–7
has not been followed so closely, but seems to exhibit the
maximum.

Microstructure.—The microstructure of the ternary alloys
corresponds very closely to that of the two binary systems;
hence it will not be necessary to present photomicrographs
covering the entire field. In the field 1–8–8, we have simple
solid solutions : as shown, for example, in Fig. 1, Plate VI.,
which exhibits the dendritic structure so characteristic of
the alloys in this field. At this magnification, the structure
has a duplex appearance ; but on examination under
a higher power, this appearance is clearly shown to be
due to the inhomogeneity of the dendritic structure. On
crossing 8–8, small islands of a grey constituent arranged
according to the prevailing dendritic structure can be seen.
This is the γ solid solution. Figs. 2, 3, and 4, Plate VI.,
show alloys which have an appreciable amount of the γ phase
present. These alloys lie about the same distance off 8–8.
From these photomicrographs the difference in structure of
cast and annealed specimens is plain to be seen ; the eutectoid
disappears with annealing. Fig. 5, Plate VI., gives the general
structure of these alloys ; Figs 6 and 7, Plate VII., the eutectoid.
As we go further into the diagram, the eutectoid is found to
increase quite rapidly, as seen from Figs. 8, 9, and 10, Plate VII.
Little change in the microstructure occurs in sections
running parallel to 7–7 until the copper-zinc side is neared.
Here the structure of the alloys with a zinc content lower
than 35 per cent. is the same as that of alloys with a higher
tin content ; and the complications due to the β breakdown
are not met with. But on increasing the zinc content,
we go over from the stable to the unstable structures (shown
by the line 1–2 in Fig. 4), passing through a zone whose
alloys usually show three constituents present. When we
reach the unstable field, the structures of the brasses are
prevalent—α needles in a ground mass of apparent β. By
noting the change in microstructure from primary α dendrites
to α segregate, we can check the location of line 5–5.

In Figs. 11 and 12, Plate VIII., the pure eutectoid structure

is exhibited. From Fig. 11, Plate VIII., we see how uniformly the inversion takes place throughout, and how the eutectoid forms colonies, much the same as the eutectic ledeburite described by Professor Benedicks; further, its similarity to pearlite is evident from Fig. 13, Plate VIII. The structure of the eutectoid with small percentages of tin is that of free β of the brasses and likewise is also not confined to a line but extends over a small, percentage perpendicular to line 7–7.

In working with the microstructure of the eutectoid and apparent β, seeking to get reproductions of them which would show the duplex structure, the author was struck with the great difficulty in actually showing that a structure is in reality heterogeneous. To the author's mind, Professor Carpenter's photomicrograph of β in his first paper is inconclusive evidence of this. Interesting in this connection are Fig. 21, Plate IX., and Figs. 22 and 23, Plate X., which represent extreme cases showing a structure known to be heterogeneous alongside of one considered to be homogeneous.

Fig. 21 shows an alloy of eutectoid composition which has been chill cast, giving an extremely fine structure, and the different tones produced can easily lead to the deduction that two constituents are present, a light and a dark one; in Fig. 22 a field is represented which overlaps the field of Fig. 21, Fig. 22 showing a coarser structure of the same specimen. A third picture (of a 5 per cent. brass), taken under identical conditions, is Fig. 23. Since a comparison of a structure known to be heterogeneous with that of a homogeneous structure fails to bring out the difference one might expect, it is clear that a photomicrograph cannot be taken as final or conclusive evidence that a doubtful structure is either heterogeneous or homogeneous.

On the γ side, we may have either $\gamma +$ apparent β in the zinc-rich alloys or $\gamma +$ the eutectoid. $\gamma +$ apparent β (with varying amounts of γ) is to be seen from Fig. 15, Plate VIII., Fig. 19, Plate IX., and Fig. 24, Plate X. The eutectoid structure is given in Fig. 26, Plate X., Figs. 17 and 18, Plate IX., and Fig. 27, Plate X.

Taking up now the microstructure of the alloys in the field

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exhibiting the two heat evolutions: in Fig. 28, Plate XI., we have an alloy of 15 per cent. tin and 10 per cent. zinc which was cooled slowly in the furnace. Three generations of α are evident: (1) the α dendrites, (2) the small α crystals between them forming an apparent eutectoid structure, and (3) the very minute α crystals in the part which appears grey. These are to be seen more clearly in Fig. 29, Plate XI. By annealing a specimen for three hours above the transformation points and allowing it to cool slowly in the furnace, the characteristic eutectoid structure of this alloy was obtained, as shown in Fig. 30, Plate XI., where the peculiar crystallization in the γ phase is conspicuously evident.

Summary.

We may sum up the results obtained in this research as follows:

1. In general, the ternary alloys of copper-tin-zinc, up to 50 per cent. zinc and 30 per cent. tin, were seen from microscopical analyses to behave similarly to the binary alloys of copper-tin and copper-zinc.

2. The liquidus surfaces, the limit of saturation of the α solid solution, and the eutectoid line were determined.

3. The eutectoid surface was found to have a maximum near the middle, corresponding to 66 per cent. copper, 17 per cent. tin, 17 per cent. zinc, and $590°$ C. on the eutectoid line. This line shows the β solid solutions to be isomorphous. Quenching from above this line produces homogeneous solid solutions.

4. The addition of tin to the brasses causes the visible breakdown of the β solid solution. The amount of the tin necessary varies with the zinc content and with the rate of cooling through the critical range. This gives rise to abnormalities in the microstructure explained on p. 23.

5. A field off the $\alpha + \beta$ range in the bronzes was found, in which two heating effects in the solid were recorded—the discussion of which is deferred for the sake of securing further evidence, especially with reference to the location of the eutectoid plane.

To Dr. Campbell under whose direction the research started, to Dr. Hanemann in whose laboratory it was carried out, and to Dr. Guertler who has taken a lively interest in the work throughout, the author expresses his sincere thanks and appreciation.

APPENDIX.

IN the paper a heating curve and photomicrographs were given for the alloy, copper 75, tin 15, zinc 10, and it was stated that off the $\alpha + \beta$ range of the copper-tin alloys, a field had been found in which the alloys showed, instead of the one transformation point of the zinc-rich kalchoids, two transformation points. This field is marked 7'-7-8-8' in Fig. 7. The investigations have been continued and the study, as here presented, has been made as thorough and complete as the limited time would permit.

The curves taken of the alloys in this region pointed to the possibility of a transformation point in the pure copper-tin alloys at about 600° C., which seems the most satisfactory explanation of this double heat effect. In the binary alloys, this upper heat effect might be very weak (an ordinary cooling curve failing to show it, see Fig. 1), but with the addition of zinc might be appreciably strengthened.

Accordingly, five alloys were made up for the purpose of studying this point, and the difference method already described was used for recording the curves. The alloys are represented by the points a, b, c, d, and e, in Fig. 7, and their curves are given in Fig. 8. These alloys all lie in the $\alpha + \beta$ range, alloy e having a composition very near the eutectoid point.

As expected, a heat effect was recorded at 590° C., very weak compared to that at 525°, but still quite perceptible. This effect is more marked as the β content increases, but when the tin content is as much as 25 per cent. it has disappeared entirely. On the assumption that this heat effect at 590° C. is in accord with the presence of a new line, the diagram in Fig. 9 was constructed. The heat effect at 590° C., then, is due to the inversion $\beta \rightleftarrows \alpha + \gamma$, and the heat effect at
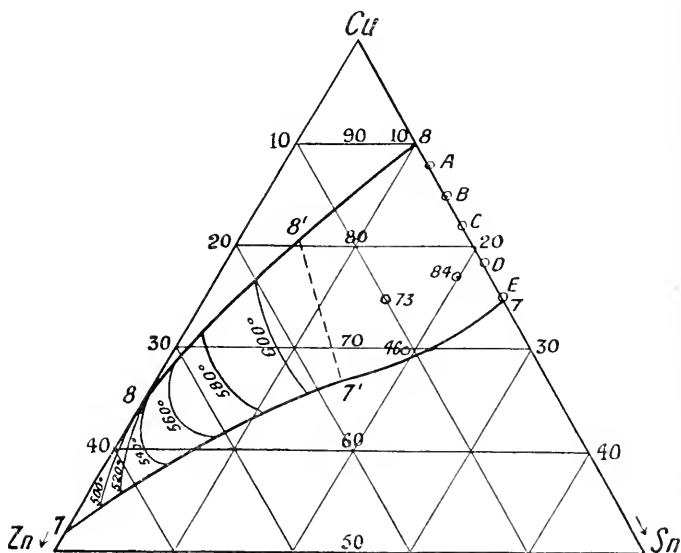
Upper plane 590°C to 608°C at maximum
Lower plane at 510°C average value

FIG. 7.—Eutectoid Surfaces.
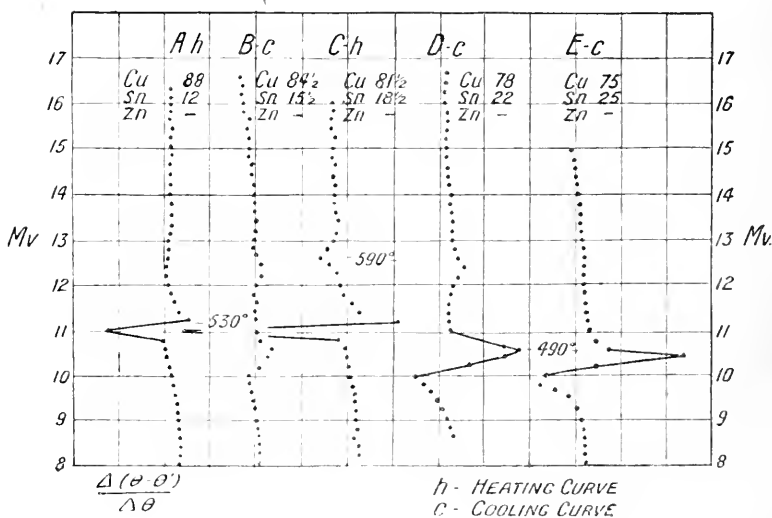
FIG. 8.

525° to the inversion $\gamma \gtrless a + \delta$. The points 2 and 3 undoubtedly lie very close to one another, inasmuch as the maximum heat effect lies toward the tin end of the line 1–3, to which fact the weakness of the effect may also be attributed. Increasing the tin content, this inversion disappears, and we have only the $\gamma \gtrless a + \delta$ inversion. A review of the literature offers no thermal evidence against such a diagram; and in fact, so far as the author knows, none of the curves taken of these alloys is so exact in nature as that obtained in the present case. Here, on both heating and cooling curves, a heat effect was noticed each time the temperature
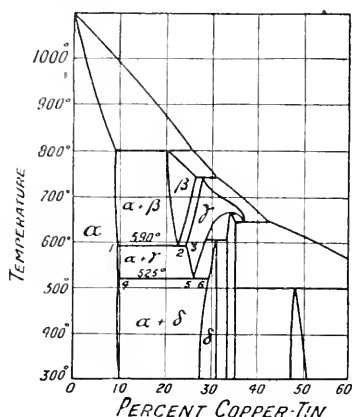
FIG. 9.—Copper-Tin.

1–3 was passed, and from the thermal evidence no discrepancies arose to make such a line 1–3 doubtful.

The addition of zinc influences these points in two ways: (1) the temperature undergoes a small rise accompanied by (2) a strong increase in the upper heat effect as compared to the lower. This rise in temperature, appreciably noticeable only after the addition of considerable zinc, is about 15° over the entire range. The upper heat effect is already strong with 3 per cent. zinc addition, as seen from Fig. 10, alloys 82, 83, and 84. Further addition of zinc causes a remarkable increase, as shown in Fig. 2 and in Fig. 10, alloy 46. Thus the upper heat effect becomes even stronger than the lower one till the latter, on reaching the line 7′–8′, disappears entirely.

The ternary system being considered as pseudo-binary, one degree of freedom is suppressed, and the transformations take place in the same manner as in the pure copper-tin alloys; hence a copper-rich solid solution will always be in equilibrium with a copper-poor solid solution. Such an assumption of course requires that the relative amounts of tin and zinc remain the same in all the phases present. The temperatures at which the transformations occur may of course vary and, as is actually the case, a maximum is attained near the
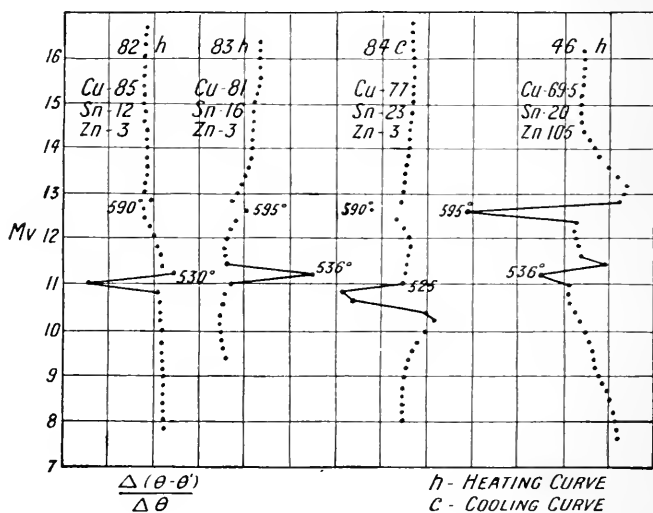
FIG. 10.

middle, at the line $7'-8'$. This is to be expected; for as the compositions of the phases vary, it is natural to have different temperatures at which saturation (separation of segregate) and mutual saturation (formation of eutectoid) occur.

A section of the diagram taken through the copper apex would resemble the diagram represented in Fig. 9; however, in it, the points $1-2-3$ and $4-5-6$ would have other positions relative to each other. This fact, and the quantitative effect of the zinc replacing the tin, cause, no doubt, the increase in the upper heat effect. That the increase of the zinc content does exercise a great influence on this heat effect

may be seen by a comparison of the curves in Figs. 8 and 10 and 2.

At the line $7'-8'$ the heat effect at $525°$ C. disappears, probably because the two phases β and β' become mutually soluble at this line.

The study of the microstructure of the pure copper-tin alloys did not support the thermal evidence toward proving the inversion $\beta \rightleftarrows a + \gamma$ at $590°$ C. Three specimens of the alloy D were heated in a small electric furnace to $675°$ C., and annealed for thirty minutes. Then, by gradually increasing the resistance, the temperature was lowered, and at $610°$ C. (thirty minutes being required for the temperature to fall thus far) one of the specimens was quenched. Again increasing the resistance, the temperature was lowered very slowly through the upper transformation point, when a second piece was quenched at $565°$ C.—it having taken thirty minutes for the temperature to drop through the $45°$ C. Then the current was switched off, and the third piece quenched at $430°$ C. The structure of these three specimens may be seen in Figs. 31, 32, and 33, Plate XI. The structure above $610°$ C. is shown to be duplex, while at $430°$ C. we have just the normal bronze structure in this range. What is quite surprising is that on passing the first heat effect (see Fig. 32) a third phase formed as a broad band around the a crystals. From this peculiar occurrence we might conclude that the upper heat effect is due to the formation of the band, and that the second heat effect is due to the breakdown of the remaining β crystals between the bands. On repeating the experiment, but annealing this time for three hours at $565°$ C. before quenching, a greater breakdown of the β constituent was produced, the grey band having grown broader and large grey islands having formed throughout the β. (See Fig. 34, Plate XII.)

From the diagram in Fig. 9, one would expect a eutectoid to form on cooling through the first heat effect, this to be followed by a second breakdown on cooling through the second heat effect. But the microstructure does not substantiate this; indeed it seems rather to indicate a very tardy formation of a single eutectoid. However, a further study of the

microstructure—as well as the thermal evidence—furnishes sufficient grounds for not accepting this fact. On passing 590° C., the formation of the grey phase occurs, the amount of it depending on the time of annealing. From Fig. 34 we see that even after three hours of annealing, the β (dark) phase is still present in large amounts, while on normal or even rapid cooling through the lower transformation point, the β disappears entirely, as seen from Fig. 33.

So far, the author has found no one diagram to explain these facts altogether satisfactorily; nevertheless the necessity of reconstructing the copper-tin diagram seems very certain. But to do this, longer annealing is required. For example, it will be necessary to anneal at a temperature intermediate between the two heat effects until stable equilibrium is reached, and then on cooling note the influence on the lower heat effect.

Micrographical experiments upon an alloy lying on the line 7–7 of Fig. 5 in the original paper showed that this line must be moved. The normal structure of this alloy on cooling is the same as that shown in Fig. 22, Plate X., which is a very fine-grained eutectoid; hence its normal structure would place it at once on the eutectoid line. However, annealing at 565° C. and quenching gives a heterogeneous and eutectoid like structure, as represented by Fig. 35, Plate XII. This would correspond to the $\alpha + \beta$ structure of the new diagram. On annealing again for forty-five minutes by gradually raising the temperature to 460° C. and again cooling, the β constituent breaks down, giving the structure in Fig. 36, Plate XII. So we see that the line 7–7′ must be shifted to suit these conditions, since a composition that corresponds to the $\alpha + \delta$ copper-tin eutectoid can have only one transformation point as alloy E, Fig. 8.

Alloy 73 behaves on thermal treatment similar to alloy D, except that under certain conditions three generations of α may form—see photomicrographs 28 and 29, Plate XI. Annealing at 560° C. for thirty minutes and quenching gives the structure shown in Fig. 37, Plate XII.—α dendrites with the β solid solution between. The thin grey border cannot be seen at this magnification. Annealing the specimen a short time at 450° C. gives the breakdown as shown in Fig. 38. Annealing

PLATE VI
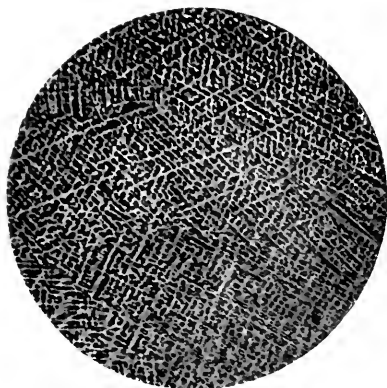
FIG. 1.—No. 7. Copper, 88·5 per cent. ;
Tin, 7·9 per cent. ; Zinc, 3·6 per cent.
Annealed at 450° C. α.
Magnification, 100 diameters.

FIG. 2.—No. 21. Copper, 78·6 per cent. ;
Tin, 9·8 per cent. ; Zinc, 11·6 per cent.
Chill cast. α – γ.
Magnification, 450 diameters.

FIG. 3.—No. 23. Copper, 72·2 per cent. ;
Tin, 5·6 per cent. ; Zinc, 22·2 per cent.
Annealed at 450° C. α + γ.
Magnification, 450 diameters.

FIG. 4.—No. 20. Copper, 66·2 per cent. ;
Tin, 4·2 per cent. ; Zinc, 29·6 per cent.
Annealed at 450° C. α – γ.
Magnification, 450 diameters.

FIG. 5.—No. 12. Copper, 78·2 per cent. ; Tin, 15·5 per cent. ; Zinc, 6·3 per cent.
Chill cast. α + γ. Magnification, 150 diameters.

Slightly reduced in reproduction.

PLATE VII
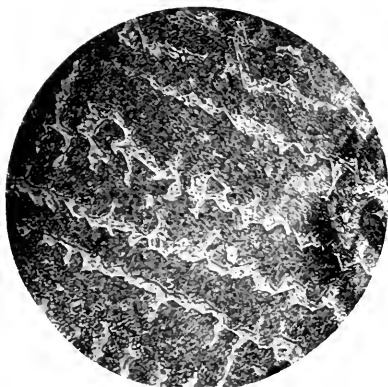
FIG. 6.—No. 12. Copper, 78·2 per cent. ;
Tin, 15·5 per cent. ; Zinc, 6·3 per cent.
Chill cast. α + γ.
Magnification, 560 diameters.

FIG. 7.—No. 12. Copper, 78·2 per cent. ;
Tin, 15·5 per cent. ; Zinc, 6·3 per cent.
Chill cast. α + γ.
Magnification, 2050 diameters.
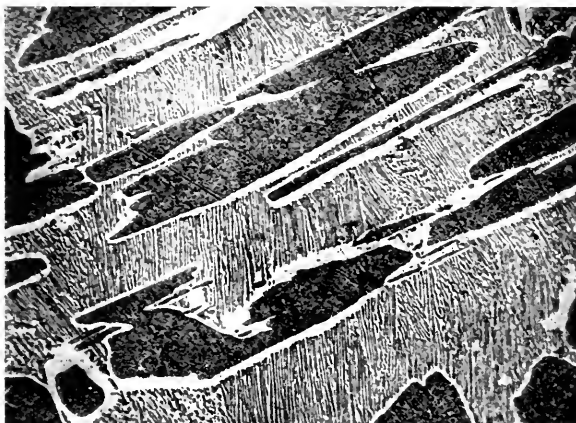
FIG. 8.—No. 70. Copper, 69·0 per cent. ; Tin, 10·0 per cent. ; Zinc, 21·0 per cent.
Slowly cooled in furnace. Primary α – eutectoid. Magnification, 360 diameters.

FIG. 9.—No. 71. Copper, 70·0 per cent. ;
Tin, 14·0 per cent. ; Zinc, 16·0 per cent.
Slowly cooled in furnace. Primary α + eutectoid.
Magnification, 150 diameters.

FIG. 10.—No. 69. Copper, 67·0 per cent. ;
Tin, 8·0 per cent. ; Zinc, 25·0 per cent.
Slowly cooled in furnace. Primary α + eutectoid.
Magnification, 180 diameters.

Slightly reduced in reproduction.

PLATE VIII

FIG. 11.—No. 68. Copper, 60·4 per cent.; Tin, 6·0 per cent.; Zinc, 33·6 per cent.
Slowly cooled in furnace. α + γ eutectoid. Magnification, 10 diameters.

FIG. 12.—No. 68. Copper, 60·4 per cent.;
Tin, 6·0 per cent.; Zinc, 33·6 per cent.
Slowly cooled in furnace. α + γ eutectoid.
Magnification, 1250 diameters.

FIG. 13.—No. 31. Copper, 61·0 per cent.;
Tin, 8·0 per cent.; Zinc, 31·0 per cent.
Chill cast. α + γ eutectoid.
Magnification, 1040 diameters.

FIG. 14.—No. 78. Copper, 65·0 per cent.;
Tin, 25·0 per cent.; Zinc, 10·0 per cent.
Slowly cooled in the furnace. γ + eutectoid.
Magnification, 40 diameters.

FIG. 15.—No. 79. Copper, 50·0 per cent.;
Tin, 10·0 per cent.; Zinc, 40·0 per cent.
Slowly cooled in furnace. γ + app. β.
Magnification, 135 diameters.

Slightly reduced in reproduction.

PLATE IX

FIG. 16.—No. 48. Copper, 66·0 per cent.;
Tin, 17·0 per cent.; Zinc, 17·0 per cent.
Slowly cooled in furnace. γ + eutectoid.
Magnification, 40 diameters.

FIG. 17.—No. 48. Copper, 66·0 per cent.;
Tin, 17·0 per cent.; Zinc, 17·0 per cent.
Slowly cooled in furnace. γ segregate
+ eutectoid.
Magnification, 210 diameters.
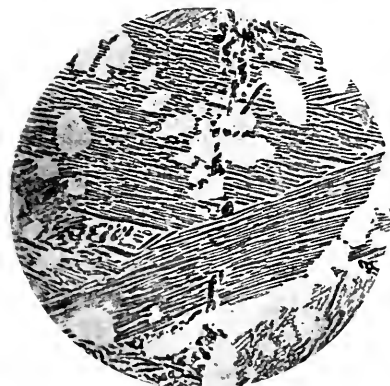
FIG. 18.—No. 48. Copper, 66·0 per cent.;
Tin, 17·0 per cent.; Zinc, 17·0 per cent.
Slowly cooled in furnace. γ segregate +
eutectoid.
Magnification, 750 diameters.

FIG. 19.—No. 6. Copper, 57·4 per cent.;
Tin, 11·2 per cent.; Zinc, 31·4 per cent.
Chill cast. γ + app. β.
Magnification, 450 diameters.

FIG. 20.—No. 6. Copper, 57·4 per cent.;
Tin, 11·2 per cent.; Zinc, 31·4 per cent.
Annealed at 450° C. γ + α.
Magnification, 450 diameters.
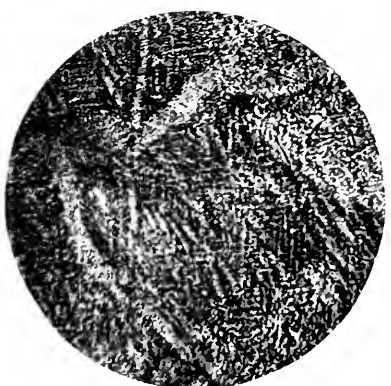
FIG. 21.—No. 34. Copper, 70·0 per cent.;
Tin, 20·0 per cent.; Zinc, 10·0 per cent.
Chill cast. α + γ eutectoid.
Magnification, 1250 diameters.

Slightly reduced in reproduction.

PLATE X
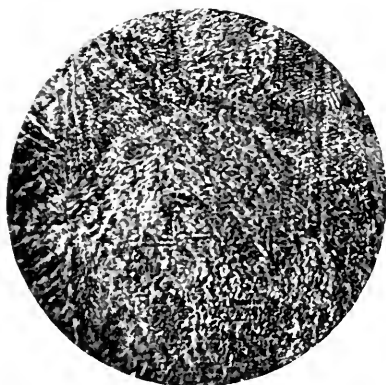
FIG. 22.—No. 34. Copper, 70·0 per cent. ;
Tin, 20·0 per cent. ; Zinc, 10·0 per cent.
Chill cast. α × γ eutectoid.
Field overlaps Fig. 21.
Magnification, 1250 diameters.
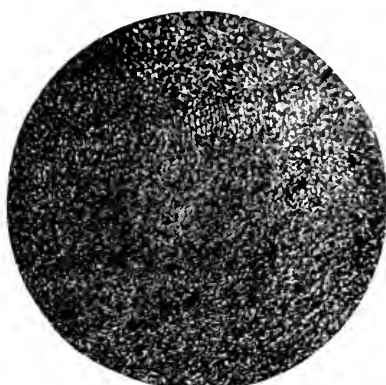
FIG. 23.—No. B, 1. Copper, 95·0 per cent. ;
Tin, 0·0 per cent. ; Zinc, 5·0 per cent.
Slowly cooled in furnace. α.
Magnification, 1250 diameters.

FIG. 24.—No. 54. Copper, 58·0 per cent. ;
Tin, 8·0 per cent ; Zinc, 34 per cent.
Slowly cooled in furnace. γ segregate – app. β.
Magnification, 700 diameters.

FIG. 25.—No. 54. Copper, 58·0 per cent. ;
Tin, 8·0 per cent. ; Zinc, 34·0 per cent.
Slowly cooled in furnace.
Magnification, 450 diameters.

FIG. 26.—No. 54. Copper, 58·0 per cent. ;
Tin, 8·0 per cent. ; Zinc, 34·0 per cent.
Slowly cooled in furnace.
β ⇄ α + γ inversion.
Magnification, 1000 diameters.

FIG. 27.—No. 78. Copper, 65·0 per cent. ;
Tin, 25·0 per cent. ; Zinc, 10·0 per cent.
Slowly cooled in furnace. γ + eutectoid.
Magnification, 700 diameters.

Slightly reduced in reproduction.

PLATE XI

FIG. 28.—No. 73. Copper, 75·0 per cent. ;
Tin, 15·0 per cent. ; Zinc, 10·0 per cent.
Cooled slowly in furnace.   α + γ (α in three
generations).
Magnification, 35 diameters.
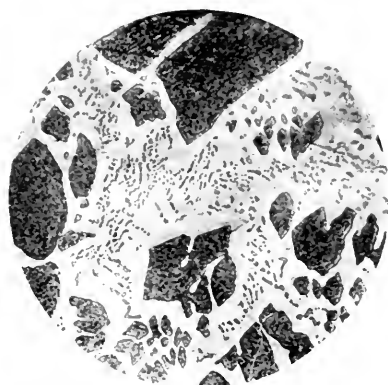
FIG. 29.—No. 73. Copper, 75·0 per cent. ;
Tin, 15·0 per cent. ; Zinc, 10·0 per cent.
Cooled slowly in furnace.   α + γ (α in three
generations).
Magnification, 1250 diameters.
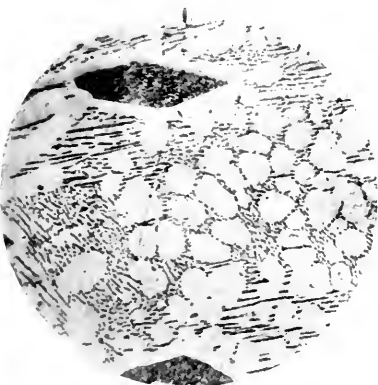
FIG. 30.—No. 73. Copper, 75·0 per cent. ;
Tin, 15·0 per cent. ; Zinc, 10·0 per cent.
Annealed at 700° C. and slowly cooled in the
furnace.   α (2nd and 3rd generations) + γ.
Magnification, 1250 diameters.

FIG. 31.—Alloy D. Copper, 78·0 per cent. ;
Tin, 22·0 per cent.
Quenched from 610° C.   α + β.
Magnification, 500 diameters.
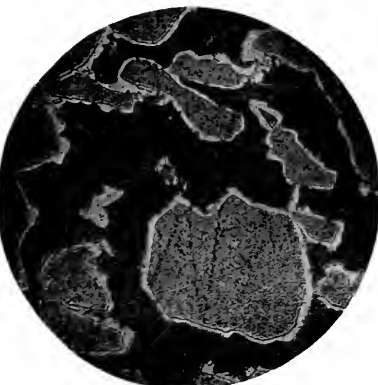
FIG. 32.—Alloy D. Copper, 78·0 per cent. ;
Tin, 22·0 per cent.
Quenched from 565° C.   Three phases.
Magnification, 500 diameters.

FIG. 33.—Alloy D. Copper, 78·0 per cent. ;
Tin, 22·0 per cent.
Quenched from 430° C.   α + eutectoid.
Magnification, 500 diameters.

Slightly reduced in reproduction.

for thirty minutes at $700°$ C., cooling slowly to $560°$ C., and quenching, gives a different structure (from that of Fig. 37), in that small a crystals have formed in between the larger dendrites, evidently the second generation earlier referred to. The structure in Fig. 29, Plate XI., offers no proof as to whether the second and third generations of a are the same phase, but inasmuch as the β phase on annealing below $545°$ C. gives a very regular duplex structure (Fig. 38), there can be no doubt that they are the same phase—a fact which must be true if these alloys are pseudo-binary.

In this appendix the author has not attempted to reconstruct the copper-tin diagram or to complete the ternary equilibrium diagram. But he has tried to show the necessity of reconstructing the copper-tin diagram as evident from certain experimental facts recorded in this research, and to suggest how this further work can best be carried out. The solution of the ternary diagram must await the corrections to be made on the copper-tin diagram. The chief points presented in the appendix are :

1. A new heat effect in the pure copper-tin alloys of the $a + \beta$ range, at $590°$ C., and

2. The location of the eutectoid surfaces as seen in Fig. 7.

DISCUSSION.

Professor HOYT, in introducing the paper, said he had every hope of being able to continue the work in future. He wished to take that opportunity of expressing his thanks, especially to his wife for her co-operation. Mrs. Hoyt knew as much about working out cooling curves, and taking pitches and everything else connected with experimental work, as he did himself.

Professor H. C. H. CARPENTER, M.A., Ph.D., Vice-President, in opening the discussion, said that as he was the first speaker on that paper, perhaps he might be allowed to offer a word of welcome to Professor Hoyt, as a new and valued contributor to their proceedings. It was hardly necessary for him to say that he found that paper very interesting. It was a case where two of them had been working some-what on the same lines, though he was afraid that he (Professor Carpenter) had been the first in the field. But they had been working very near to one another. As Professor Hoyt pointed out on page 243, he was actually engaged in that troublesome piece of micrographic work, the resolution of the pure β constituent into α and γ when his (Professor Carpenter's) paper appeared. To his mind the most interesting discovery came at the very end of the paper, where the research had been left in an unfinished state. Professor Hoyt had found that there was distinct evidence of a new inversion in the copper-tin series. The evidence had presented itself to the author in some ternary alloys, where he found on the copper-tin side of the ternary diagram that he obtained not one inversion in the solid state at about $590°$ C. but two, the lower one being at about $525°$. It was naturally very interesting to in-vestigate the copper-tin series further, and, as Fig. 8 showed, three of the curves appeared to agree in indicating that there was a new inversion in that series. It was absent from the first alloy and also from the last alloy, that is to say, from the alloys nearest the boundaries of the phase fields, and it was strongest in the two central alloys. From that Professor Hoyt concluded that he had obtained a horizontal line running across the diagram which, as explained in Fig. 9, was at $590°$, and he proceeded on that assumption to point out that that was an indication of another possible inversion in the β and γ constituents. The microscope did not support that view. He was going to suggest quite tentatively, and he had discussed the question with Professor Hoyt the day previously, a possible explanation of that inversion. He approached the matter from experience gained in his (Professor Carpenter's) laboratory with the copper-aluminium β constituent, and the work which Mr. Andrew, his demon-strator, had been doing would be published shortly. Mr. Andrew had found something very similar in investigating the influence of a third metal on the copper-aluminium β constituent. He also found that with ordinary rates of cooling he got two inversions in the alloy. He found, further, that if he took one of those ternary alloys, and heated it up above the upper point, and then cooled and held it just below that

point, then the lower inversion point disappeared altogether, showing that it was due to super-cooling of the upper inversion. Possibly, if Professor Hoyt had held his alloy D for more than three hours at 560°, and had then taken a curve, he might have found the lower change point absent altogether. That would be a simplification of the diagram, and it would indicate only one change and not two. He thought it would be a very interesting investigation to carry out. If that interpretation was correct, then 525° represented the limit of super-cooling, and the proper temperature of the inversion was 590°.

He was particularly interested in the resolution of the β constituent. It was a matter of very great practical interest. Professor Hoyt found that with pure, or very nearly pure, copper-zinc alloys, it was extremely difficult to resolve them into the eutectoid structure. His diagram Fig. 4 was of considerable importance, because it indicated the extent to which tin could be dissolved without causing any appreciable segregation of the γ constituent. His photographs of the inversion were very beautiful, and he would like to compliment Mrs. Hoyt and the author upon them. In particular, he would like to refer to the resolution near to the copper-zinc side of the diagram. As Professor Hoyt pointed out, some of the structures, in his (Dr. Carpenter's) own later paper particularly, did not show the eutectoid inversion. That was quite true with regard to the eutectoid structures of the lamellar type, but if they took Fig. 12, which represented the alloy cooling at the ordinary rate in the furnace, there they had obviously the eutectoid structure. Taking the alloy to which he himself had referred, Fig. 19, γ plus β, there annealing broke down the lamellar structure, and obviously gave a good deal more γ, and so caused irregularity. That was not the eutectoid structure, but rather indicated the breakdown of the β to γ and a. Those were the chief points he had to raise, and he hoped that Professor Hoyt would find time to conclude that investigation, which he had left in so interesting a condition. He would also like to compliment him on the great experimental skill he had shown.

The PRESIDENT said that before they went any further with the discussion, he would like to state that Sir Cecil Hertslet, His Majesty's Consul-General for Belgium, who was stationed at Antwerp, had very kindly paid them a visit, and he would ask him now to address them before going further with the discussion.*

Dr. W. ROSENHAIN, F.R.S., Member of Council, resuming the discussion on Professor Hoyt's paper said that he had not very much to say about it, because it dealt with a system of alloys upon which personally he had done very little work, and his interest was merely that of a reader, who was very pleased to see that complicated system of alloys being further worked out. Besides expressing his appreciation of the paper and his congratulations to Professor Hoyt for making so splendid a contribution to their proceedings, on the first occasion that

he had so favoured them, he wanted to deal with only two really side issues connected with the paper. The first related to the manner adopted for the presentation of the results. Of course he knew the reason for it, because the paper was a fairly long one, and considerations of economy naturally suggested a certain amount of abbreviation, and that the presentation of such a work should be in the briefest possible form. He was inclined to think it was a great pity that policy was adopted, and he would have been very glad indeed to have seen a very much fuller statement of the data. They were told that a certain thing was done, but they wanted to know how those observations had been made and the conclusions determined, and they were only given a very few cooling curves. A diagram, however well founded it might be, was none the less a conclusion drawn by the author. It was information based upon data which might be perfectly sufficiently justified. Nevertheless the details of the observed facts and the statements of observed facts were comparatively few. The result might be extremely intelligible and interesting, but it was not all they wanted, and his reason for stating that was that particularly in the country to which Mr. Hoyt was proud to belong, it had become customary to publish work in a far less satisfactory manner than the system adopted in England. It seemed to be thought to be enough to put in curves and set out an equilibrium diagram on the take-it-or-leave-it principle. They were willing to take it, but he would rather have the matter worked out than have the feeling that it was necessary to reinvestigate any of those diagrams, so as to see if any of the facts needed correction. He, on one occasion, had to spend five or six months in repeating an investigation which would have been to some extent unnecessary if the earlier work had been adequately published, and he appealed to all concerned with the presentation of papers to give them the whole facts as fully and as clearly as possible, so that they could trace where the investigator was accurate or otherwise. To take as an example, the suggestion that the lower inversion might possibly be due to incomplete reaction at a higher temperature. It would be possible, if the matter had been put fully before them, to have determined whether that was possible or not, by an inspection of the cooling curves.

The second point he wanted to make was one of considerable interest to the Institute, because it gave him (Dr. Rosenhain) an opportunity of reminding them that they had at present sitting a committee dealing with the question of the nomenclature of alloys, and as Chairman of that Committee he was interested in the question of nomenclature and particularly in the term used in the title of the paper. He had only seen that paper since he had been out of England, and not having had an opportunity of looking up a Greek dictionary, he had not been able to find out how it was arrived at. He referred, of course, to the term "kalchoids." It might be the best possible term to use for the copper-tin-zinc alloys, or it might be very undesirable. He would ask all those who were interested in the question of nomenclature, either in the written discussion of the paper or verbally, and either to him-

self or to the secretary, to express their opinion on the use of the term kalchoids, and so to make it a sort of example as to whether the introduction of words of that kind was desired or would be tolerated by makers, users, and workers in metals. That Institute was the proper vehicle by means of which such an opinion could be ascertained, and it would be of the greatest possible service to get an opinion as to whether the use of the word was justified by the facts. However, the word had been passed by the Publication Committee of the Institute, but the desirability of its permanent use was still an open question, and he would be glad if they could get some guidance as to the use of the word in the paper.

Dr. W. GUERTLER (Berlin) said that he thought that if a practical man were to read that paper, he would very likely think "that man may be all right, and it is quite interesting, but I don't see the use of it. I see a certain number of curves going backwards and forwards, but what is the sense of it." He thought that if a paper of this kind did not convince the practical man they could not help him. Like papers which had been given by Dr. Rosenhain on copper, manganese, and aluminium, and by Professor Carpenter on aluminium and zinc, that paper furnished a very good proof of the practical value of purely theoretical investigation, and showed how it was possible with least expenditure of time so to conduct investigations on theoretical lines, that the information thus obtained would enable one not only to predict what qualities were to be expected from the various systems, but also in what special relative proportions of the mixture the qualities were to be found. The eutectoid structure was eminently important because it was very fine, and it furnished the reason why steel, for example, was so enormously valuable, because it derived from its eutectoid its wonderful mechanical properties. Professor Carpenter had shown that such a eutectoid in its very fine state, was found also in the brasses just as in bronzes, but in the latter it was much coarser. That was why the bronzes, although having the same relative amount of eutectoid, had not the same mechanical properties, and would not show the same tensile strength. In this respect Professor Hoyt's experiments had had very remarkable results, though the data presented here might not be quite sufficient to prove them. Yet he (Dr. Guertler) could say from his personal acquaintance with those experiments that Professor Hoyt had at least proved beyond any doubt, that all those copper-rich copper-tin-zinc alloys all behaved in exactly the same way as the two binary systems, because of the very interesting fact that the β and γ series formed solid solutions and the ternary β solid solutions all showed the same breakdown into a and γ at certain temperatures. Only the a and β phases of the system had practically valuable properties. Therefore one need only give special attention to the fields of a and $\beta = (a + \gamma)$. Furthermore Professor Hoyt found that under normal conditions the tin would render the very fine eutectoid structure of the brass coarse, as soon as the percentage of tin amounted to a few per

cent.   This explains the sudden breakdown, found long ago, of the mechanical properties, which breakdown was caused by the same additions of tin.   The question what properties might be expected from copper-rich copper-tin-zinc alloys was now answered, and it was needless to hunt for tough alloys among those poor in copper.   Further research might confine itself to brass with the addition of only a few per cent. of tin.

As to the copper-tin diagram, a new thermal effect was discovered, at the very last minute, which was very interesting.   But it could not be definitely explained.   Professor Carpenter had already said that perhaps on annealing at temperatures between the two thermal effects the lower one would be suppressed.   He (Dr. Guertler) agreed with that, but he thought there might be another reason.   If one took Fig. 32 one would see those black parts, which were brown in reality, were β, and one would notice those medium dark ones, which were α, and between the two one would see part of the new phase coming out which looked brown.   If one annealed that alloy one would get the Fig. 34 in which the brown borders were increased.   Professor Hoyt had annealed the specimens still longer, which again increased them.   A picture of that kind proved absolutely beyond any doubt that by reaction of the two phases with each other a new phase was formed, and so the position in the constitution diagram of those two phases which were formerly β and α must be to the left and right of that new phase forming the new boundary which was light in colour.   That brown phase was certainly new.

From the microscopic evidence it seemed to be the same as the δ which formed after the last breakdown of the γ, and so one might think that the homogeneous field of the δ-phase had to be shifted to the copper side, and would lie to the left of the β-γ crystals.   The first suggestion that offered itself was that the new phase might be the β or γ crystals, as there was no possibility of finding any microscopical evidence of a difference between the two, but after the aforesaid this explanation had to be renounced, and that old question about the behaviour of β against γ must again be left to the future.   It might be expected that later on it would be proved that the δ really lay to the left of the β and γ.   If that were true, a double thermal effect would be found under normal cooling conditions.   The first effect was due to the formation of the δ, and if one cooled lower down one got a second effect by the breakdown of the rest of the γ.   If the equilibrium was established, no γ-phase could be found to the left of the composition of the δ-phase, because only the two phases α and δ could there be present in a state of equilibrium.   Now it was clearly seen from the picture in Fig. 32 that such synthetic reaction $(\alpha + \gamma = \delta)$ could not easily be completed, as the δ formed a wall between the two other components, and so blocked the reaction that it was only after very long annealing that the reaction could reach equilibrium, one could understand that δ and some γ would be left, and that that γ would cause a thermal effect by its breakdown even to the left of the δ-phase.   Now if one annealed until one got equilibrium, the reaction $\alpha + \gamma = \delta$ would come to an end, and the thermal effect would be

found to the right side only and not to the left side. This ought to be a crucial test to settle that question. It was very important from the theoretical side, because it would give quite a new aspect to the questions of the annealing of those bronzes, and this effect would be a very strong one because very long annealing would produce quite different properties by slowly completing the formation of δ. However, he hoped that Professor Hoyt would settle that very interesting question.

Mr. O. F. Hudson, M.Sc. (Birmingham), said there was just one point he might say a word about, and that was the question of the very extraordinary behaviour of the β-phase in the copper-zinc series. He had spent many months worrying that phase in all sorts of ways, and trying to make it break down by annealing it alone, in the presence of an excess of γ, and in the presence of an excess of α, but on no occasion had he ever been able to get the slightest sign of any breakdown of the β to give α and γ. He thought it very well worth remembering that this was a most extraordinary structural stability. There was no doubt, of course, that a change did occur, but for all practical purposes, when dealing with the pure copper-zinc alloys, he thought they might take it that the β-phase behaved as a perfectly stable material.

The President (Professor A. K. Huntington, Assoc. R.S.M.) said he would like to bear his testimony to the very great amount of work in the paper. When it first came under his observation he was surprised at the enormous amount of work it represented, and he thought they did not quite realize its extent. They must not be surprised that Professor Hoyt had not had time to work it out to the last detail, as he would wish to do. They hoped he would go on with the work and worry the β and other phases a little more when he got back to America. When it came before him as Chairman of the Publication Committee, he observed the feature which Dr. Rosenhain had pointed out, that there was not sufficient detail as regards the experiments, and he pointed out to Professor Hoyt that deficiency, asking if he could possibly furnish fuller detail. But they realized the position the author was in. He did not want to make the paper too cumbersome, and it was exceedingly difficult to know where to draw the line on the question of giving detail. They quite appreciated his position. At the same time he thoroughly endorsed what Dr. Rosenhain had said as to the difference in the value to the Institute, to science generally, as well as to practical men, of a paper with or without sufficient detail. That value must be greatly reduced if they did not get a certain amount of detail of the experiments, and it entirely prevented one taking up that line of investigation. He had experienced it constantly himself. It prevented the taking up of work in such a way that they knew where they were. It was impossible to take up work where the other man left off, and if they had to investigate everything it meant a waste of time and very likely they did not do the work at all, and so they were checked in their investigation. He hoped they might induce Professor Hoyt in a little

appendix to give somewhat more detail with regard to the curves and observations in time for publication. That would greatly enhance the value of the papers, and he hoped they would support him in trying to induce the Professor to do it.

Mr. C. BILLINGTON (Longport) said that from the practical point of view the alloys were not of any commercial value, and he could not understand why they were used without at the same time comparing the results obtained with a well-known commercial alloy in each class of alloys to which reference was made. If they took the alloy under discussion, copper 78 per cent., tin 22 per cent., or copper 70 per cent., tin 20 per cent. and zinc 10 per cent., neither of these could be used in practical work and their only value, to his mind, was that they furnished a record of behaviour of fancy mixtures under certain conditions ; but if papers like Professor Hoyt's were to deal with useful everyday alloys as well, they would be of much more interest and value to the practical man in foundry work. At the same time he would admit that no doubt some of them might throw light on the weaknesses sometimes found in alloys now in common use by exaggerating such defects, but the defects referred to should be shown to exist in the useful alloys at the same time.

Mr. F. JOHNSON, M.Sc. (Birmingham), said that he would like to add his tribute of appreciation to that expressed by previous speakers of the remarkable effort of Professor Hoyt in bringing forward that paper. The remarks of the last speaker called to his mind some experiments he had performed on commercial alloy, viz. brasses containing small quantities of tin. No doubt the fact would be recognized that those alloys stood in a class of their own, and in some respects were superior to the brasses themselves. He thought some of the experiments detailed in that paper, although many of them were entirely of a theoretical nature, brought out points of extreme importance to the practical man. For example, on page 245, Professor Hoyt gave a cooling curve of a copper-tin-zinc alloy in which he showed the temperature of the eutectoid inversion, and that was exceedingly important to the manufacturer of copper-tin-zinc alloys. That alloy might not be a commercial one, but the temperature of the inversion was the same in the commercial alloy. For the purpose of annealing metal it was extremely important for a manufacturer to know that temperature, as Professor Hoyt had recorded it there. He could the more readily affirm that because as a matter of fact he had recorded it in a paper which he (Mr. Johnson) had read before the Institute of Metals, Birmingham Local Section. He recorded that temperature as being about 590° C.,* the alloy in question being composed of 70 per cent. copper, 25 per cent. zinc, and 5 per cent. tin.

There was another point to which he would like to briefly refer, viz.

* *Metal Industry*, Feb. 1913, p. 75.   The temperature was 595° C. on the heating curve and 560° C. on the cooling curve.

the determination of the composition of the 100 gramme alloys in connection with the cooling curves. They were weighed before and after the preparation of the alloys, and the loss in weight was attributed to the volatilization of zinc, but if borax had been used as a cover, as in the experiments with smaller ingots, some loss of copper must have occurred. He would suggest to Professor Hoyt that that method of determining the composition could not be regarded as satisfactory.†

Professor HOYT, replying on the discussion, said that he would like to express his thanks for the criticism offered, and for the welcome he had received. In particular, he was grateful to Dr. Guertler, who had induced him to apply for membership. There were one or two words he would like to say in conclusion about the second transformation point in copper-tin alloys. The effect might possibly be due to the presence of illuminating gas, used as a neutral atmosphere in all cases, and he did not know for certain that the gas had not affected the copper-tin alloys in that respect. He had not heard of that, or read of it in any literature on the subject, but it would be of material importance if it were so.

With regard to the β-phase, perhaps, as Professor Carpenter suggested, it was unstable over a certain range. That would account for the fact that in literature there was recorded a wide range of temperature for the lower transformation. If they examined the diagrams they would find some giving the curve at $470°$, and others at about $500°$, while in one case $525°$ was given, which was also verified by his own experiments.

With regard to what Dr. Rosenhain said about insufficient data, he must admit that it reminded him very much of the criticism which was brought out by Carpenter and Keeling in 1904. There was a cry then raised, both in England and France, why did he not give more data ? Personally, he had no objection to give data in a paper like that. There was no doubt it would increase its value, but it would also have increased its size so tremendously that he was shy of including it all in the present paper. With regard to presenting his data either in an appendix or in another paper, he would be very glad to do that if opportunity presented itself.

With regard to Dr. Rosenhain's criticism of the use of the term " kalchoids," he (the speaker) was very innocent in selection of the term and could not claim any credit for originating it. He always used it in his own writings, but he first met with it in a book by Thurston on copper-tin alloys. That author used the term " kalchoids," and he (Professor Hoyt) very innocently used it also. He accepted the term because he did not know anything better ; but he would be glad to have any opinion bearing on the subject.

He would like to say a few words in answer to Mr. Billington on the practical value of the work. Of course work of that kind was neces-

† [The speaker has since written to point out that even if a carbonaceous covering had been used, some loss by oxidation was almost unavoidable, and although the error thus introduced might not be very serious, it would have been advisable to have checked some of the alloys by chemical analysis.—ED.]

sarily very extensive, and he was almost compelled to restrict himself to results having a direct bearing on the particular problem at hand. With regard to the practical value of the paper, he supposed the practical man would judge the value of such a paper on the information given as to the various temperatures and the effect of time and temperature on the alloys, and how these affected the various properties of metals which they actually used in their work. No doubt a manufacturer would like to look at the paper, and, after he had read it, to say, " I have found out *this*, and I can give *these* instructions to my men how to handle their metals." That might or might not be possible, but he hoped at least to have given enough to increase the general knowledge of the practical man in regard to those alloys. He did not believe a man could study those subjects without being better qualified for practical work. Take. for example, the case of steel. He did not think there was a practical man in any steel works or engaged in the manufacture and production of the better grade steels who did not consider it absolutely necessary to understand the nature of steels and their constitution. Formerly, the manufacturer did not consider this necessary, but the division between theory and practice had broken down, so that it was almost impossible to say " this is theoretical but that is practical." Why should not that diffusion of theoretical and practical knowledge be extended to other alloys. In that way it was possible to circulate knowledge as to the constitution and behaviour of alloys. for the help and guidance of the practical man.

A METHOD OF IMPROVING THE QUALITY OF ARSENICAL COPPER.*

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INTRODUCTORY.

In ' reading the discussion on Webb's paper, " Locomotive Firebox Stays," † the author was greatly impressed by the contribution from the late Mr. S. W. Johnson, from which he quotes the following extract :

" Owing to increasing steam pressures, higher firebox temperatures, larger fireboxes, and heavier work, the stays of locomotive fireboxes were very severely strained and heated in the more modern types of locomotive ; and this fact was now calling the serious attention of locomotive engineers to the question of staying, and causing them to look out for a more suitable material than commercial copper . . . it was not merely a question of ductility and strength. The material must stand the action of heated gases without suffering corrosion ; its coefficient of expansion must be such that it expanded and contracted with the copper box into which it was screwed, so as not to set up leakage ; it must be soft enough to stand riveting without damaging the threads in the copper plates, and sufficiently flexible to stand the differential expansion of the box and shell without fracture. Copper more or less pure had so far served remarkably well, but it remained to be seen which alloy of that metal was really the most suitable for staying locomotive fireboxes."

Believing that the chances were remote of satisfying these requirements by making large additions to copper of other metals, particularly in face of the experiences of Webb and Johnson with copper alloys, the author took the view

that if copper had served so remarkably well it would be a profitable investigation if some means could be found of improving the quality of the metal without sacrificing those properties which rendered it such a suitable material, viz. co-efficient of expansion, softness for riveting, flexibility, ductility, and strength.   If some of these properties could be improved without lowering the standard of the others, and if that wastage which occurs in service as a result of the action of heated gases—some of them of a reducing nature—could be lessened, then a material would have been produced more nearly approaching the ideal than ordinary commercial copper.

Appreciating the value of arsenic both to the manufacturer and to the user, the author regarded it as an indispensable ingredient, particularly in view of its influence in decreasing the power of copper to dissolve gases and thus enabling sounder metal to be cast.   The problem was to produce an arsenical copper free from cuprous oxide and also free from those injurious elements such as bismuth which, as the author has shown,* may be harmless in "tough-pitch" copper, but which would ruin oxygen-free copper.

As has been well proved by Heyn,† Archbutt,‡ Bengough and Hill,§ and others, the action of a reducing gas such as hydrogen upon "tough-pitch" copper at or above $600°$ C. is to render it brittle, and in common with Archbutt, T. Johnson,‖ &c., the author believes this brittleness to be due to the abstraction of oxygen, and to the intercrystalline weakness engendered thereby.   Proof of this theory will be found in the following pages.

To produce then an oxygen-free arsenical copper requires the use of a deoxidizing agent which shall fulfil the following requirements :—

1. It shall, in addition to completely removing oxygen, help to remove gases to such an extent as to ensure soundness in the castings.

* *Journal of the Institute of Metals*, No. 2, 1910, vol. iv. pp. 163–234.
† *Zeitschrift des Vereines deutscher Ingenieure*, 1900, vol. xliv. p. 508.
‡ *The Analyst*, 1905, vol. xxx. p. 385.
§ *Journal of the Institute of Metals*, No. 1, 1910, vol. iv. pp. 34–53.
‖ *Proceedings of the Birmingham Metallurgical Society*, 1906.

2. It shall not form a harmful combination with arsenic.

3. It shall not cause any degeneration in the essential properties of the metal as enumerated above.

4. It shall not interfere with the working properties of the metal, even if present in considerable excess of the quantity requisite for deoxidation.

5. It shall be cheap.

As a further reason for wishing to produce such an improved copper, the author recalls an occasion when the desirability of doing so on a commercial scale appealed to him rather forcibly. " Tough " copper wire had been purchased by a manufacturer of copper rivets and, in one consignment, he received wire which had been made from a brand of copper rather richer in impurities than usual. This meant that the proportion of oxygen had to be higher, so much higher in fact that the copper was embrittled and would not stand the severe cold work imposed in the process of forming the head.

After a number of experiments of a tentative nature the author found that silicon could be added to arsenical copper in considerable excess of the quantity required to effect deoxidation without producing hot-shortness.

Little or no work of a similar nature appears to have been done, although it has been long realized that silicon is an element which can be added to high-conductivity copper for the purpose of improving its quality without seriously lowering its electrical conductivity.* T. Johnson † found that the conductivity of electrolytic copper was lowered from 101 to 99·7 per cent. by the addition of ·004 per cent. silicon, whereas the same quantity of phosphorus lowered the conductivity to 98·5 per cent.

As, however, the property of electrical conductivity is of no importance in tough arsenical copper, the special value of silicon in this respect has played no part in the author's investigations.

PRODUCTION OF BARS.

In order that no objections might be raised on the score of expense, a ferro-silicon of high silicon content was chosen,

* Thurston, " Materials of Engineering," Part III., Alloys, Brasses, and Bronzes.

† *Proceedings of the Birmingham Metallurgical Society*, 1906.

as it was deemed inadvisable to introduce much iron into the copper. As the results of the experiments show, however, that iron is a welcome ingredient, it would probably have been more advantageous to have chosen a ferro-silicon of 60 to 65 per cent. silicon, on account of such an alloy having a melting point in the neighbourhood of 1250° C., *i.e.* considerably lower than that of the alloy chosen by the author. It was with considerable difficulty that the ferro-silicon could be introduced into molten copper, and consequently a special copper-iron-silicon alloy was prepared and used for making the necessary additions. This " addition " alloy had a low melting point and was readily dissolved by the molten copper.

Preparation of the Ingots.—The copper was melted in a graphite crucible under charcoal, the correct quantity of copper–arsenic alloy added to give the requisite amount of arsenic, and finally the weighed portion of the copper-iron-silicon alloy.

The molten alloy was then stirred and poured into ingots in the manner described in a former paper [*] by the author.[†]

These ingots were rolled under conditions also outlined in that paper, and the resulting bars ($\frac{1}{2}$-inch diameter) were submitted to the various tests.

The analyses of the bars are given in Table I.

Table I.

No. of Bar.	Copper per Cent.	Arsenic per Cent.	Silicon per Cent.	Iron per Cent.	Oxygen per Cent.	Total.
S0	99·61	0·34	0·02	0·035	nil	100·005
S1	99·37	0·36	0·20	0·06	nil	99·99
SS2	99·36	0·36	0·15	0·07	nil	99·94
S3	99·28	0·39	0·22	0·13	nil	100·02
S4	99·10	0·38	0·36	0·13	nil	99·97‡
S6	98·56	0·35	0·80	0·24	nil	99·95
U1	...	0·37	nil	0·05	nil	...
U2	98·89	0·69	nil	0·43	trace	100·01
E	99·59	0·344	nil	nil	0·066	100·00
R	99·905	nil	nil	nil	0·089	99·99

* *Journal of the Institute of Metals*, No. 2, 1910, vol. v. p. 174.

† On account of the " piping " which was caused by the introduction of silicon, and due at least partly to its " degasifying " influence on the metal, it was found advisable to cast most of the ingots on end and reject the piped portion. Ingots U1 and U2, however, were cast flat.

‡ Bar S4 was produced from an ingot which had of necessity to be remelted on account of an accident when pouring. The ingot before remelting contained 0·44 per cent. silicon and 0·20 per cent. iron. It will be seen that there has been a greater percentage loss of the iron than of the silicon. The remelting was effected under a cover of charcoal.

It is interesting to note that both silicon and iron have a strong deoxidizing influence on copper, and that when they are added together the silicon is the more efficient, as the relative proportions of the two in the "addition" alloy and the ingots prove.

Rolling Properties.—Without a single exception the ingots behaved admirably during the hot-rolling.   As the proportions of silicon and iron increase, a slight increase in the working hardness is noticeable.

Methods of Analysis.—The methods of analysis for copper and arsenic were similar to those described in the paper to which reference has just been made, whilst silicon and iron were determined by the usual gravimetric methods, care being taken to separate arsenic from the ferric hydrate precipitate in the iron determinations.

The analyses of bars E and R are included in Table I. for the purposes of comparison, E being a "tough-pitch" arsenical bar and R a "tough-pitch" high-conductivity bar free from arsenic.

Mechanical Tests.

Tensile Strength and Ductility.—The test-pieces were turned down for a gauge-length of 3 inches to $\frac{3}{8}$-inch diameter.

Table II.

No. of Bar.	Arsenic per Cent.	Silicon per Cent.	Iron per Cent.	Tensile Strength. Tons per Sq. Inch.	Elongation per Cent.		Remarks.
					On 3 Inches.	On 1 Inch at Fracture.	
S0	0·34	0·02	0·035	15·55	43	...*	Elastic limit,† 6·7 tons
S1	0·36	0·20	0·06	15·60	50	68	...
SS2	0·35	0·15	0·07	15·85	40	...*	Elastic limit,† 6·7 tons
S3	0·39	0·22	0·13	16·30	37	60	...
S4	0·38	0·36	0 13	16·20	41	60	...
S6	0·35	0·80	0·24	18·25	37	56	...
U1	0·37	nil	0·05	16·15	46	66	Elastic limit,† 7·1 tons
U2	0·69	nil	0·43	17·05	48	67	Elastic limit,† 7·3 tons
E	0·34	nil	nil	15·70	41	52	Oxygen, 0·066 p. cent.
R	nil	nil	nil	14·92	39	...*	Oxygen, 0 089 p. cent.

* Broke outside gauge points.

† Yield point not well defined.   The figures given refer to the first noticeable elongation.

The results are given in Table II. It will be as well
to state here the reason for the inclusion of bars U1 and
U2, which were made in an exactly similar manner to the
other bars, with the exception that no silicon was introduced,
a copper-iron alloy (containing 10·2 per cent. iron *) being
used in order to introduce iron. On reference to Table II. it
will be seen that the increase in tensile strength is far more
a function of the iron than of the silicon where both are
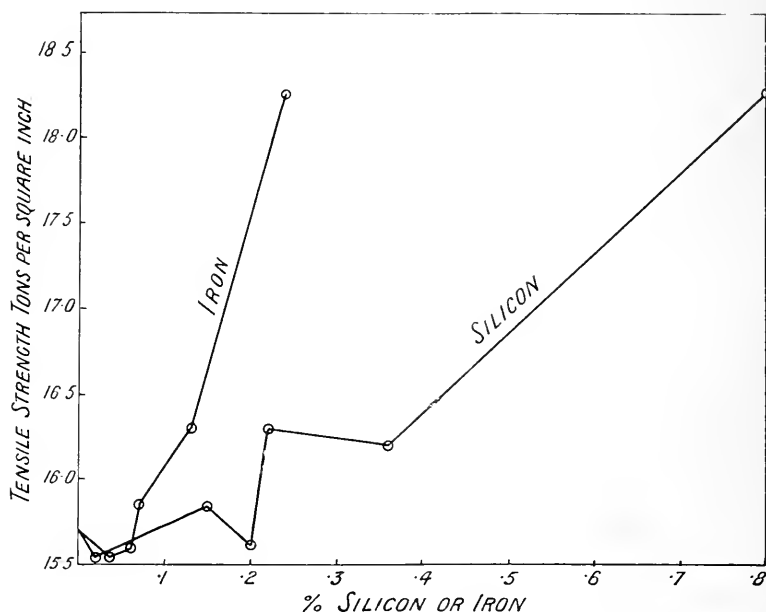
Fig. 1.

present. This is very graphically shown when the percentages
by weight are plotted against tensile strength, as shown in
Fig. 1.

Taking iron alone, a much smoother curve is obtained than
by taking silicon alone, and although these curves have an
entirely fictitious meaning, since the increase is purposely
attributed in each case entirely to the influence of one element,

* This alloy was made from electrolytic copper and Kahlbaum's pure iron wire. The
fracture of the cast alloy was little different from that of pure copper in colour and texture.

whereas it is really due to a combination of the two, yet they bring out clearly the fact that iron has a greater strengthening influence than silicon.

It was therefore decided to verify this by making arsenical bars containing iron and no silicon. Bars U1 and U2 show clearly the strengthening influence due to iron *per se*. It will be noticed that in the low-silicon bars (S1 and S0) the tensile strength is lower than that of the " tough-pitch " sample E. This is mainly attributable to the removal of oxygen, which is known to have a strengthening effect, but in view of the fact that iron is also present it would seem possible that the initial influence of silicon is to soften copper, an influence which has to be counteracted by some of the iron before the strengthening influence of the latter can assert itself. This point requires confirmation, but a comparison of bars U1 and S1 is significant. Bar U1, with 0·05 per cent. iron, has a tensile strength of 16·15 tons, whereas bar S1, with 0·06 per cent. iron and 0·20 per cent. silicon, has a lower tensile strength, viz 15·60 tons.

These points, however, are of minor consideration for the moment, and it will be as well to review the results at this stage in so far as they affect the requirements which the author laid down in an earlier portion of the paper.

Of the five requirements enumerated, it will be seen that four have been already completely satisfied, either by the addition of silicon and iron together or by the addition of iron alone. That is to say, the additions have :

1. Yielded deoxidized ingots perfectly sound and free from porosity.

2. No harmful combination with arsenic has been produced.

4. The working properties of the metal have not been interfered with even when the added elements have been present in considerable excess.

5. The added material is cheaper than copper itself.

The third requirement is a very comprehensive one, since no degeneration in the following essential properties is allowable, viz. coefficient of expansion, softness for riveting, flexibility, ductility, and strength.

The figures given in Table II. show that not only have the properties of strength and ductility suffered no degeneration, but in some instances have been considerably improved.

The coefficient of expansion of the bars has not been determined, but as the composition is so little changed from that of commercial " tough " copper, it is safe to assume that this property has undergone no appreciable change.

No riveting tests have been carried out, but the malleability of the bars in the cold is of such a high order—in fact much superior to " tough-pitch " copper—that the behaviour of the specimens in any such test may safely be assumed to be excellent.

There remains the property of flexibility, which the author prefers to term toughness. This has been tested by the resistance offered by $\frac{3}{8}$-inch round test-pieces to alternating

TABLE III.—*Alternating Stress Tests on the Arnold Machine.*

No. of Bar.	Arsenic per Cent.	Silicon per Cent.	Iron per Cent.	No. of Alterna-tions.*	Gain in Tough-ness per Cent.	Appearance of Fracture. Texture.	Appearance of Fracture. Position of Tension Line.
S0	0·34	0·02	0·35	223	17	Silky and even	Central.
S1	0·36	0·20	0·06	243	33	Do.	Do.
SS2	0·35	0·15	0·07	256	35	Do.	Do.
S3	0·39	0·22	0·13	239	25	Do.	Do.
S4	0·38	0·36	0·13	258	36	Do.	Do.
S6	0·35	0·80	0·24	182†	...	Do.	Central, but accompanied by slight flaw.
U1	0·37	nil	0·05	211	...	Do.	Central.
U2	0·69	nil	0·43	244	33	Do.	Do.
E	0·34	nil	oxygen 0·06	190	...	Silky and even, but not quite so lustrous	Do.
R	nil	nil	0·08	182	...	Do.	Central, but broader than the others.

* Mean of two tests.   † Low result probably due to flaw.

stresses. The tests have been very kindly carried out for the author by Dr. Arnold in his testing-machine at Sheffield University. The results are given in Table III., and it will

be noticed how splendidly the bars have behaved in comparison with the "tough-pitch" arsenical bar E and the "tough-pitch" electrolytic bar R.

Taking bar E as a "tough-pitch" standard, there is an increase in toughness in four of the bars ranging from 25 per cent. to 36 per cent., only one, viz. S6, showing any inferiority. This inferiority was probably due to a flaw in the specimen resulting from the rejection of insufficient of the "piped" portion of the ingot, and possibly to the finishing temperature being rather low.

The fractures of all the kinetic test-pieces from S0 to U2 were more silky and lustrous than that of bar E ("tough-pitch" standard). They all displayed a remarkable evenness of texture, while the colour became paler and paler as the percentage of silicon increased.

In a single bending test all the rolled bars bent over through $180°$ without cracking.

BEHAVIOUR OF BARS UNDER THE INFLUENCE OF A REDUCING-GAS AT HIGH TEMPERATURE.

The gas chosen for the tests was hydrogen, being produced in a Kipp's generator and well washed and dried before passing over the specimens heated in a silica tube to a temperature of $780°$ C. The specimens measured $\frac{3}{8}$ inch diameter by 2 inches,

TABLE IV.—*Results of Tests on Specimens heated to* $780°$ *C. for two hours in Hydrogen.*

No. of Bar.	Oxygen per Cent.	Arsenic per Cent.	Result of Bending Test.
S0	nil	0·34	Bent through $180°$. No cracking
S1	nil	0·36	,, ,,
SS2	nil	0·35	,, ,,
S3	nil	0·39	,, ,,
S4	nil	0·38	,, ,,
S6	nil	0·35	,, ,,
U1	nil	0·37	,, ,,
U2	trace	0·69	,, ,,
E	0·056	0·34	Broke with ut bending
R	0·089	nil	,,
X	0·026	0·52	,,

and were maintained at the high temperature for two hours, being allowed to cool in an atmosphere of hydrogen.

The accompanying table (Table IV.) gives the results of the bending tests on the specimens thus treated, and in Fig. 2 a number of the tests are shown.

These results show that it is oxygen in copper, either in the presence or the absence of arsenic, which renders it susceptible to the disintegrating influence of reducing-gases at high temperatures.

The author considers that the experiments which have been described have borne results which justify him in stating that a means has been found for improving the quality of arsenical copper as regards its mechanical properties, its working pro-
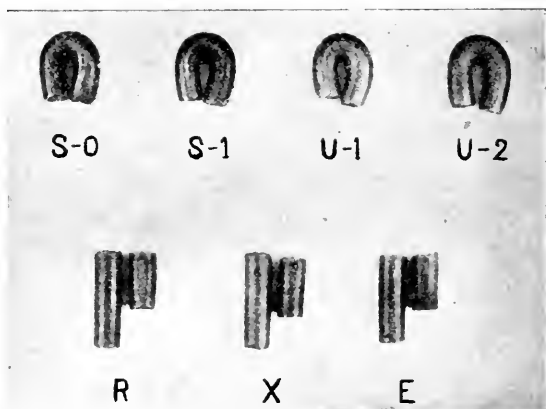
FIG. 2.
(*See Table IV., p.* 283.)

perties, and its immunity from " gassing," and in all probability, therefore, its ability to withstand for a longer time the action of heated gases.   To obtain this improvement there has been no lowering of the standard in other directions.

From a commercial point of view there are two possible objections, viz. :

1. The necessity for using pure copper.   The author has used electrolytic copper in his experiments, but he has also experimented with some of the purer brands of refined American Bessemer copper and found them to give good results.

2. The production of a " pipe " in the ingots treated with

silicon or iron. Whilst this " pipe " leads to the production
of more scrap than in the case of " tough-pitch " copper, the
improved quality and greater soundness of the metal more
than compensates for this disadvantage.

In order to test the practicability of the method on a larger
scale, the author received the consent of Mr. L. Sumner, M.Sc.,
of the Broughton Copper Company, Limited, to have trial
billets cast.

Electrolytic copper was used, and after melting down in
graphite crucibles under charcoal, the necessary amounts of
metallic arsenic and copper-iron-silicon alloy were added and
stirred in. The metal was poured into solid cylindrical billets,
one of which was subjected to fluid compression.

Works' Tests.

Table V.—*Tests on a Commercial Scale.*

Approximate Weight of Billet.	No. of Rolled Rod.	Composition.				Tensile Strength. Tons per Sq. Inch.	Elongation per Cent. on 2 Inches.	Contraction of Area per Cent.	No. of Alternations.		Remarks.
		Cu.	As.	Si.	Fe.				Annealed.	Un-annealed.	
100 lb.	BR 1	98·74	0·34	0·08	0·81	16·14	63	81	336	270	Billet un-pressed when cast.
180 lb.	BR 2	99·27	0·36	0·05	0·31	15·34	70	85	272	231	Billet pressed when cast.

N.B.—The tensile tests were made on 1-inch diameter annealed rod, whilst the alternating stress
tests were on $\frac{3}{8}$-inch diameter specimens turned from the 1-inch rod.

The results of tensile and alternating stress tests, together
with the analyses, are given in Table V.

The figures given in Table V. show that there are no diffi-
culties in the way of applying the author's results in practice.
They also show that a metal of superior quality can be pro-
duced. Mr. Sumner reports that the billets rolled in a manner
similar to ordinary " tough " copper. No application of the
method to a big charge of copper in a reverberatory furnace

was essayed, but the author has no doubt that such an application is quite feasible.

Referring to Table V., the powerful influence of iron is again demonstrated, especially when it is pointed out that rod BR1 was produced under less favourable circumstances than BR2, the latter having had the advantage of fluid compression when cast. Moreover the billet was much heavier than BR1, and in order to produce the finished rod (1-inch diameter) a greater amount of " work " was necessary, and this would tend to improve the mechanical properties. The superior composition of BR1 has, however, conferred better properties in spite of these handicaps.

The author does not regard fluid compression as a necessary operation in casting copper for rolling, except in such a case as this, where the effects of " piping " may be mitigated. It then resolves itself into a question of economy, viz., the possibility of the cost of fluid compression being compensated for by the saving of scrap caused by piping.

Tests at High Temperatures.

In order to test the behaviour of the material at high temperatures the author had tensile specimens prepared and sent to Mr. George Hughes, Chief Mechanical Engineer of the Lancashire and Yorkshire Railway Company at Horwich, who very kindly had them tested at high temperatures under the conditions outlined in his paper,* presented at the Newcastle Meeting. Unfortunately, however, the author was under the impression that the rod received by him was in the condition in which it had been submitted to the tensile tests by the Broughton Copper Company. Such was not the case, however, the rod from which the specimens were turned for Mr. Hughes' tests being in a semi-hard condition. The results of the high-temperature tests are therefore not comparable with the tests at normal temperature as given in Table V. There was only a small piece of rod BR2 left, and the author had this turned down and tested at normal temperature in

* " Non-Ferrous Metals in Railway Work," *Journal of the Institute of Metals*, No. 2, 1911, vol. vii. pp. 74-120.

order to give some meaning to the high-temperature test.   The results are given in Table VI.

Results of tensile tests on three of the smaller experimental bars are also given.   The percentage losses of tensile strength are similar, thus showing no superiority on the part of the tough-pitch oxygen-bearing bar E.   A slight fall in elongation is also noticeable throughout.

TABLE VI.—*High-Temperature Tests.*

No. of Bar.	Temperature. Degrees F.	Dimensions. Inches.	Tensile Strength. Tons per Square Inch.	Elongation Per Cent. on 2 Inches.	Contraction of Area. Per Cent.	Percentage Loss of Tensile Strength.
BR 2	Normal	1×0.66	19·4	*	...	...
BR 2	400	3×0.66	16·7	23·5	70·6	14
BR 1	300	3×0.66	18·1	25·0	77·6	...
E	400	3×0.375	12·4	39·0	74·4	21
SU 2	...	...	13·1	34·0	81·8	23
S 3	...	...	12·8	34·0	80·7	21

* Specimen had only 1 inch gauge-length.

MICROSTRUCTURE.

All the bars of Table I. were examined and found to possess structures in the hot-wrought condition quite similar to that of bar E, with the exception that none of the characteristic " oxidules " were present in bars to which the deoxidizing addition had been made.

The examination of the bars after annealing in hydrogen yielded interesting results.   In the case of the bars which were ruined by this treatment it was observed that the " oxidules " appeared black under the microscope, due to the reduction of the Cu_2O to amorphous metallic copper, the light blue colour observable under usual conditions having completely disappeared.   After etching it was noticed that a network of cracks was most conspicuous in the structure, this network probably marking the original crystalline boundaries of the cast metal, since the cracks did not seem to follow twinning planes, nor the " wrought-crystal " planes produced as a result of mechanical work (see Fig. 7).   The cracks were doubtless produced by the generation of steam as a result of the reaction $Cu_2O + H_2 = Cu_2 + H_2O$ (steam).

An examination of BR1 rod (see Table V.), as rolled, showed that the original " cores " had not disappeared, although a very uniform wrought-crystalline structure had been produced.

The micrograph (Fig. 3) shows the structure of a longitudinal section of BR1.   Traces of the original " core " structure are distinctly visible.   The micrograph (Fig. 5) shows the same section under higher power.

Figs. 3 and 4 show the marked difference between a longitudinal and a transverse section of a rolled arsenical bar in which

FIG. 3.—Bar BR1 as rolled.   Longitudinal.
Vertical illumination.   Etched.
Magnified 70 diameters.

FIG. 4.—Bar BR1 as rolled.   Transverse.
Magnified 150 diameters.   Etched.

equilibrium has not been established.   The alternating dark and light streaks in Fig. 3 are due to the elongation of the metal in rolling and drawing before the original " cores " of the cast metal have been obliterated by annealing.   The appearance of the smaller crystals accompanied by much " twinning " afford further evidence that considerable " work " —followed by annealing—has taken place.

In a transverse section (Fig. 4) these crystals predominate in the microstructure, the long drawn out " core " threads

not appearing so pronounced when cut transversely, although visible in some parts of the section.

Fig. 5 is a micrograph from the same section as Fig. 3, but under higher power. The crystals show some elongation due to cold-drawing, and slip-bands are visible mainly in a direction at right angles to the direction of drawing. After half an hour's annealing at $850°$ C. the "cores" had almost disappeared and no slip-bands were visible. Figs. 6, 7, and 8

FIG. 5.—Same as Fig. 3. Shows slip-bands (due to cold "work") at right-angles to direction of drawing, which is from left to right.

Magnified 250 diameters.

FIG. 6.—Bar S0. Longitudinal. After 2 hours in hydrogen at 780° C. Magnified 250 diameters.

show the microstructures of bars S0, E, and R respectively, after similar treatment in "gassing" and in polishing and etching.

Fig. 6 is typical of all the S and BR bars after similar treatment. It should be noticed that the crystals are not excessively large, that no cuprous oxide nor intercrystalline cracks are visible, thus explaining the superiority of the bars over bars containing oxygen and subjected to the same treatment. All the bars upon which experiments have been carried out contained their impurities—arsenic, silicon, and

T

iron—in the state of solid solution. A marked difference is to be seen between the structure of the arsenical " tough pitch " bar E and the non-arsenical bar R. In both cases the intercrystalline disintegration is apparent, but the great crevices and cracks which appear in the copper-oxygen bar are not apparent in the arsenical bar. Whether this may be due to the larger proportion of oxygen in bar R (0·08 per cent.), as compared with that in bar E (0·06 per cent.), is not certain, since it
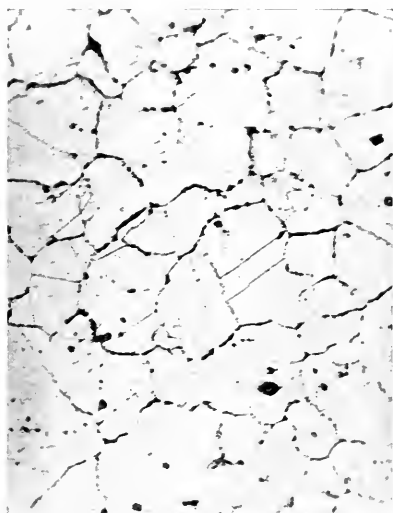
FIG. 7.—Bar E (Arsenic 0·36 per cent., Oxygen 0·06 per cent. Longitudinal. After 2 hours in hydrogen at 780° C.

Magnified 250 diameters. Etched.

FIG. 8.—Bar R (Oxygen 0·08 per cent.). Longitudinal. After 2 hours in hydrogen at 780° C.

Magnified 250 diameters. Etched.

must not be forgotten that the cuprous oxide in arsenical copper has a different structural arrangement from that in pure copper. This will be seen from an examination of Figs. 9 and 10, which represent the structures of copper-oxygen and copper-arsenic oxygen alloys respectively. The coalescence of cuprous oxide under the influence of arsenic in hyper-eutectic alloys has been demonstrated by Law.* This coalescence is now shown to be true in the case of hypo-eutectic

* *Journal of the Institute of Metals*, No. 2, 1912, vol. viii.
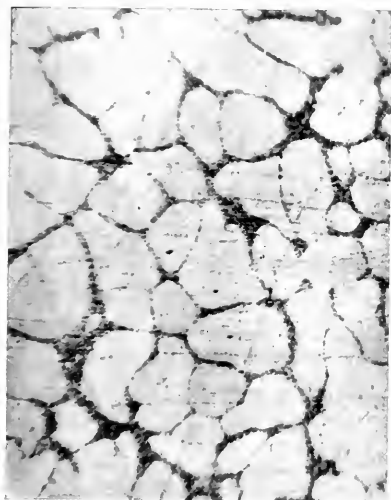
FIG. 9.—Cast copper containing 0·2 per cent.
oxygen. Shows continuity of eutectic.

Magnified 150 diameters.

FIG. 10.—Cast copper containing 0·19 per cent.
oxygen, 2 per cent. arsenic. Shows isolat-
ing effect of arsenic on Cu_2O particles.

Magnified 150 diameters.

FIG. 11.—Bar U2 as rolled.
Magnified 250 diameters. Etched.

alloys, and therefore in copper of commercial composition.
In a previous paper by the author the isolation of the cup-
rous oxide globules in arsenical copper is to be seen.*   With-
out entering into a consideration of the improvement in
mechanical properties of the copper effected by arsenic (and
they are indisputable) the author thinks that the greater
degree of rottenness of the " gassed " non-arsenical bar (R) may
be due in some measure to the structural continuity of the
copper-cuprous oxide eutectic, which would seem to offer an
easier passage to the inroads of reducing-gases.   It will be
noticed that the black patches in Fig. 7, which represent
spaces occupied originally by globules of cuprous oxide, are
not confined to the crystalline boundaries whence the gaseous
products have made their escape, but are contained in some
instances within the crystals themselves.

Fig. 11 shows the structure of bar U2 as rolled.   The high
arsenic and iron contents of this bar account for the very
pronounced " coring," which is plainly visible to the naked
eye, and which is not entirely obliterated by the two hours'
annealing in hydrogen.

It will be noticed in this as in other bars that twin crystals
appear although the metal has not been subjected to any
cold work.   The " core " structure is visible in all the other
arsenical bars as rolled, but not to so marked an extent.

Vertical illumination was employed in every case.

Conclusions.

1. A method has been discovered of deoxidizing and con-
ferring soundness upon cast arsenical copper.

2. The rolling properties of the metal have not been im-
paired, in fact an improvement in cold malleability has been
secured.

3. Even if present in considerable excess, the added elements
have no injurious effects.

4. None of the properties considered to be essential in
commercial " tough " copper for locomotive stay-rods have
suffered degeneration.

* *Journal of the Institute of Metals*, No. 2, 1910, vol. iv., Plate X., Nos. 5 and 6.

5. The toughness of the metal has been increased.

6. The resistance of the metal to the influence of a reducing gas at high temperatures has been secured.

The expenses entailed in carrying out the foregoing experiments have been met by a grant from the Royal Society.

It is with great pleasure that the author records his acknowledgment of the invaluable assistance rendered to him by Professor Arnold, D.Met., of Sheffield University; Professor Dixon, M.Sc., Birmingham University; Mr. George Hughes, M.Inst.C.E., of Horwich; and Mr. L. Sumner, M.Sc., of Manchester.

DISCUSSION.

Sir GERARD MUNTZ, Bart., Past President, in opening the discussion, said that in the previous papers they had been rather on the pinnacle of high science, and he had listened with great interest and gathered such information as he was able to absorb therefrom. But now they had come once more down to the level of the practical man where, personally, he would feel very much more at home. He would like to say a few words about that paper. Beginning at p. 276 the author said, " If some means could be found of improving the quality of the metal without sacrificing those properties which rendered it such a suitable material, namely, coefficient of expansion, softness for riveting, ductility, flexibility, and strength—if some of those properties could be improved without lowering the standard of the others . . . a material would have been produced more nearly approaching the ideal than ordinary copper." He quite agreed with him, but Mr. Johnson was thirty-five years behind the times. He did not want to say anything unkind about the paper, but, before he (Sir Gerard) went into the business thirty odd years ago, that had been done. It was not only done, but continued to be done, and was being done at the present time, not merely in samples, but in 100-ton lots, so that that paper seemed to be, although extremely interesting, rather late in the day. The paper was specially interesting to himself, probably having had more experience of that class of work than anybody else in the manufacturing world.

There were some points in which he was not quite in agreement with Mr. Johnson. The paper would have been more useful and valuable if he had left the little matter of arsenic out, and named it " A Method of Improving the Quality of Copper." He (Sir Gerard) held the opinion that arsenic in copper was not only valueless but detrimental. Its only object was as a deoxidizer. He had long since left off using arsenic in copper, as an unintelligent and old-fashioned method, never to be used when it could be avoided, and, in fact, only used by those who did not know how to employ better and more intelligent methods. He did not believe in putting anything in that was of no use, and arsenic certainly was no use, except as a deoxidizer, and they could deoxidize equally well and produce quite as good results by other means, such as, for example, by the addition of silicon, aluminium, or phosphorus, which did very much less harm. In casting copper, if arsenic were used, they were much more liable to get an occlusion of gases than they were without it. For many years, the treatment of copper with various additions had been a daily experience of him, and he was certain that a better, stronger, more ductile copper could be produced without arsenic than with it. To give them some idea that he was talking with good reason, he might tell them that in the year 1879, before he was in the business, his company, Muntz's Metal Company, supplied to the London & North-Western Railway Company a set of copper locomotive tubes of specially deoxidized copper, which were practically tested by the late F. W. Webb, who at the time was locomotive superintendent of that

railway. That set of tubes was put to work on express train work, and ran 486,000 train miles before they were discarded after eighteen years' work. That was rather phenomenal, because the ordinary run of a copper tube was about 150,000 miles, or 200,000 miles. It would be considered an extreme case to go beyond 220,000 miles. Those tubes did not contain arsenic. When set to work they weighed 2 tons 4 cwt. 3 qr. 9 lb., and when taken out they had lost 15 per cent. in weight. The analysis of the tubes was as follows :—Copper, 99·767 per cent. ; silver, 0·008 per cent.—the copper, they would see, was rather high ; iron, 0·0015 per cent. ; nickel, 0·102 per cent. ; sulphur, 0·007 per cent. ; then there was a residue of phosphorus, 0·045 per cent. ; and an oxygen content of 0·0102 per cent. The results of a test of that material made, not by themselves but by the London & North-Western Railway Company, were as follows :—

Temperature of Test.	Tensile Strength, Tons per Sq. Inch.	Elongation on 2 Inches.	Contraction of Area.
Degrees F.	Per Cent.	Per Cent.	Per Cent.
60	18·64	29·0	81·9
300	17·04	24·5	84·4
500	14·96	23·5	81·9
700	11·52	21·0	63·5

It was essential in the making of copper that it should not be easily affected by high temperatures, and he thought they would agree that those were very remarkable results. Those tests were taken by Messrs. Nash, of Sheffield. There was really very little to say in favour of arsenical copper when they looked at those tests.

That deoxidized copper, Muntz's No. 1 Special, was also tested by the late Mr. Drummond, who was at the time locomotive superintendent for the London and South-Western Railway, on behalf of the Central South African Railway, who placed an order for locomotive fire-box stays of that material. The rods tested were 1 inch diameter, and screwed from end to end ; they were vibrated through one-eighth inch, one-sixteenth inch to either side. The length of stay free was $3\frac{3}{4}$ inches. It was tested cold, and the rod broke after 1579 vibrations. When tested at 375° F. the rod broke after 1190 vibrations. The rods were tested unannealed as supplied for use. It would be noted that they were 1 inch diameter and screwed from end to end. Mr. Johnson did not state the length of alterations used in his tests, and it would be of interest to know that. But if they would compare those figures with the figures given by Mr. Johnson, they would find that there was very little to be said in favour of arsenical copper even as low as 300°. He proposed to compare the tests given by Mr. Johnson for tensile and elongation. The only one fairly comparable was the test at 300° F., when they found the following results :—

Johnson's.	Temperature of Test.	Tensile Strength, Tons per Square Inch.	Elongation on 2 Inches.	Contraction of Area.
	Degrees F.	Per Cent.	Per Cent.	Per Cent.
BR 1 . .	300	18·1	25·0	77·6
U 2. . .	300	17·1	34·0	81·8
Muntz's No. 1.	300	17·0	24·5	80·4

There was not much in favour of the arsenical rod, and it was harder and more likely to distort the holes in the fire-box plate. A number of tests had been made for them by Messrs. Nash, at their Sheffield testing works, on an alloy, " Muntz's nicro " copper-nickel, at varying temperatures, which gave the following results :—

Temperature of Test.	Tensile Strength, Tons per Sq. Inch.	Elongation on 2 Inches.	Contraction of Area.
Degrees F.	Per Cent.	Per Cent.	Per Cent.
60	15·84	62·5	76·8
300	15·55	58·2	78·1
500	14·54	60·0	78·1
700	13·84	56·0	76·5

It was of interest to notice how well that nickel alloy retained its strength and ductility even at temperatures as high as 700° F. Both those classes of material were largely used, and were becoming more popular year by year. Hence his opening remark that Mr. Johnson's suggestion was somewhat belated. In his own experience, they were continually doing quite as well without arsenic as with it. He quite agreed as to the great desirability of reducing the oxygen. In most other respects he was fully in accord with Mr. Johnson's contentions, though he doubted if with silicon and arsenic satisfactory results could be commercially attained on a large scale in commercial practice. In Table I., Mr. Johnson showed six samples of copper without any oxygen. All he (Sir Gerard) could say was, he did not believe any man could attain that perfection practically on a large scale with any continuity.

Mr. F. Tomlinson (Manchester) said that in the first place he would like to express agreement with Sir Gerard Muntz when he said that the author's work was not new. His firm had also used similar methods for the past ten or fifteen years or more.

He would like to be quite clear on this question, and tell the author that they had made laboratory experiments some ten years ago with exactly the same object as the author's, *i.e.* to produce an arsenical copper which would not be affected by the action of reducing gases at high temperatures.

One method employed was to melt the copper, and add the desired amount of arsenic in an atmosphere of hydrogen. The results obtained were practically the same as those described by the author.

Somewhat similar results were also obtained by the use of deoxidizers such as phosphorus, silicon, magnesium, &c. In their experiments the best results in this direction were obtained when using hydrogen.

The author had mentioned a firm as having given some assistance. He had the pleasure of being a member of that firm which rendered assistance in the carrying out of some of these tests; but at that time he was not quite clear as to the object of the author's experiments, otherwise he would have been very pleased to have laid before him the results of the similar experiments just referred to.

The previous speaker (Sir Gerard Muntz) had questioned the advisability of using arsenic in copper; these views came rather as a surprise. He had not come prepared to discuss this question, but in his opinion the isolated quotation of the behaviour of a set of tubes did not carry much weight. He had not had so many years' experience in the copper world as claimed by Sir Gerard; but possibly he had had greater experience with the smelting and refining of large charges of tough arsenical copper, and also the subsequent working up of this copper into the form of tubes, plates, and rods, &c., for locomotive and marine engineering requirements. His experience had been so consistently favourable that it would not permit of his faith being the least shaken in arsenical copper. Every engineer who used that class of copper would say it had been a good servant to him, and he was sure they would take a lot of moving from that position. Sir Gerard's sympathies were evidently with non-arsenical copper, but this is entirely against the long experience of many large users of tough arsenical copper, and it is the user who must decide such questions.

Any further remarks he had to make would be in form of written communication.

In conclusion, he wished to say that he hoped to have the pleasure on some future occasion of seeing the author again at the works, and when he would be pleased to place at his disposal a considerable amount of information bearing on the subject of his paper.

Mr. H. H. A. GREER (Glasgow) said that during the last twelve months he had had a good deal to do with the question of use of copper with arsenic, aluminium, and so on. The firm with which he was connected some time ago bought a large quantity of copper pipes that had been salvaged from the gunboat *Montagu*, which, they would remember, was ashore at Lundy Island. They sold a quantity of these tubes to a large firm, who utilized them for making castings. One of these castings was a large condenser, and he was invited to see it. The whole of that condenser, right down from one side to the other, was broken with one huge crack. This condenser was 8 tons. They examined the metal, and on analyzing found that there was from $1\frac{1}{2}$ to 2 per cent. of aluminium, showing that, when this was mixed up with the tin, the result was very

detrimental, and no doubt that alloy was responsible for the serious defect on the casting. He thought that was a warning to people when buying old material. It cost his firm a good few pounds before they got the matter settled up. He discovered, on inquiry, that the Admiralty had been experimenting at the time the *Montagu* was built with aluminium, because they thought that that alloy would toughen the copper and make it more suitable for its requirements.

The PRESIDENT (Professor A. K. Huntington, Assoc.R.S.M.) said that he would like to point out with regard to the test pieces, they had not been specially annealed to any standard, and, that being so, they got more work on one than on another, and so it was not possible to make comparable results where there was a difference of half a ton or a ton more work applied. That might very easily occur, and sometimes they might get a difference of several tons due to different work on the test pieces. It was really impossible to compare them unless they were annealed to some common standard. He did not consider that in the Summary No. 6 "the resistance of the metal to the influence of the reducing gases at high temperature had been secured," had been proved by any of the experiments referred to in the paper; they could only be assured of that after practically using the metal for a considerable time. There was nothing more difficult than to understand what was going on in the case of stays. He did not wish to labour the point, but he thought it right to say they must receive with some caution statements based upon a few experiments such as they had in the paper.

Mr. F. JOHNSON, replying to the discussion, said he very greatly appreciated the contribution to the discussion by Sir Gerard Muntz, because that was a contribution by an authority to which they all paid respect. Sir Gerard had given exceedingly interesting figures, although he had stated that he (the author) was thirty-five years behind the times. In regard to that he would venture to assert that the information given by Sir Gerard had never before appeared in print.

Sir Gerard Muntz interposed to remark that some of them had been published in a publication issued by the firm, though not for general distribution.

Mr. Johnson, continuing, said he would contend that if the figures resulting from his own investigation confirmed what was known even a thousand years ago, but only known privately, they were no less valuable.

Sir Gerard (continued the speaker) proceeded to make an attack on the statement that arsenic was a beneficial addition to copper. It would take a long time to go into the various details required to prove the addition of arsenic to be beneficial, but that could be done, not only from his own experiments, but from the recorded results of practical users. He contended that arsenic did,—in fact he knew it did,—neutralize the injurious influence of impurities such as, notably,

bismuth. He had perfect proof of that, and in fact he had proved it in a previous communication ; and he was quite ready to prove it again. It certainly did not act as a deoxidizer, and proof of that was to be found in the fact that the addition of arsenic to copper containing oxygen caused no sensible diminution in the quantity of oxygen. When put into molten copper, arsenic prevented gases from going into solution, and therefore that explained Sir Gerard's term "densifier." The figures given by Sir Gerard referred to tubes made under contract, and made from very much larger ingots than those with which he (the author) had been able to experiment, but it was not with the object of comparing the figures in the paper with the figures that were capable of being obtained in practice, that those figures had been given. They were really given for comparison among themselves, and solely to illustrate the principles embodied in the paper. A small bar made from an ingot ten pounds weight, twenty pounds weight, or even a hundred pounds, could not be compared with a tube made from an ingot or billet weighing perhaps half a ton.

Sir Gerard Muntz remarked that the ingots he had referred to weighed one hundred pounds.

Mr. Johnson said that even so, in the case of a tube very much more cold work would be put upon it, than in the case of a bar worked in a hot state which would not have the same mechanical properties as were conferred by cold work, nor could cold-worked material be compared with hot-worked material, which had had merely a superficial drawing to give it a smooth surface.

In the remarks of Mr. Tomlinson results were given relative to the production of arsenical copper free from oxygen which it was said was not at all a new material. There again, he would repeat what he had already stated, that if that was only known privately, and not to the members of the Institute, a service had been rendered to the members by placing those facts before them. It was very useful to have the facts before them, and to have the results of definite experiments carried out with a definite object. Mr. Tomlinson had mentioned that oxygen-free copper had been produced by melting in an atmosphere of hydrogen. Probably he did not wish to suggest that that should be put forward as a commercial proposition ? (Mr. Tomlinson : Oh, no.) The same speaker had mentioned other deoxidizers which had the same beneficial influence as silicon. Some of them had the disadvantage, *e.g.* phosphorus, that if they existed in excess they caused brittleness, and others, *e.g.* aluminium, if added to arsenical copper, disagreed with the arsenic and also produced brittleness. But, so far as he knew, no experiments of a similar nature had been made, bringing out the facts now published. He was glad to hear that Mr. Tomlinson's faith was not shaken in arsenical copper, but it was remarkable that here they had two authorities quite at variance with one another, yet each was an expert whose opinion must command respect. It was a question they would all like to see thrashed out. Personally, he agreed with Mr. Tomlinson that arsenical copper was an exceedingly useful material.

Mr. Johnson, continuing, said Mr. Greer's remarks were very interesting and very amusing. The remarks by Professor Huntington implied that the results given in some of the tables could not be legitimately compared with results obtained in practice.

The President, interposing, said his point was that unless the annealing was done in some definite way, bringing everything to a common standard, they could not compare tensile tests. There were bound to be little differences in the amount of work, and that would be sufficient to account for getting higher or lower tensile results, and therefore they could not say that because they had such and such a thing that was because of the difference in composition. It was quite impossible to get comparisons unless they brought everything to some common standard.

Mr. Johnson said that point was brought out in a paper which he had presented in 1910,* and in which the results of tests of bars in the hot-worked condition had been compared with the results of tests of the same series after cold-working and annealing under conditions which brought them to the common standard which the President had indicated as desirable.

The increase in strength indicated by the former set of tests as being due to an impurity (bismuth) had been confirmed by the second set of tests.

COMMUNICATIONS.

Professor A. K. HUNTINGTON, Assoc. R.M.S., President, wrote that he had used silicon and iron in copper alloys for more than thirty years, and for more than twenty years in fire-box stays, both as deoxidants and ultimate components. Thousands of tons of such material for which he was responsible had been used during that time. This had not been done privately, as patents had been taken out at various times. He was very familiar with the effects of iron on copper, having made many hundreds of tests of such material. He thought it would be as well that these facts should be put on record. He had no objection to make to the paper other than what he had said at the meeting.

Mr. F. TOMLINSON (Manchester) wrote in further reference to Sir Gerard Muntz's remarks concerning the merits of tough arsenical copper compared with a copper of high degree of purity. He (Mr. Tomlinson) recognized that purer copper, whether deoxidized or not, assaying say over 99·5 per cent. up to practically 100 per cent., had a large field of utility in the production of the numerous copper alloys, and also in the manufacture of copper wire, bars and strips, or other forms of copper where high electrical conductivity was of first importance, but such copper was not the most suitable for other purposes where the best possible mechanical properties were the first consideration.

* *Journal of the Institute of Metals*, No. 2, 1910, vol. iv. p. 233.

During the last twenty years, commencing with Second Report of the Alloys Research Committee by Professor Roberts-Austen, much research and practical investigation has been carried out with copper both in this and other countries. The evidence of such investigations, backed by the practical experience of all leading locomotive and marine and general engineers, had given overwhelming proof in favour of the use of *tough arsenical copper* for all purposes when the best mechanical properties and power to resist corrosive and erosive influences were of prime importance. For such purposes the presence of a definite amount of arsenic in copper had proved to be of equal importance to the presence of the correct amount of carbon in steels to be used for certain specific purposes.

As denoted by Sir Gerard Muntz, investigation had not been confined to arsenic. Much work had been done in the direction of substituting elements other than arsenic, such as various deoxidizing agents—nickel, iron, aluminium, &c.—with a view of improving the mechanical properties. That work, in most cases, had been confined to the production of comparatively small lots of metal obtained by melting in crucibles, which admitted of the easy addition of deoxidizers and other ingredients, and products had been turned out which gave very good results in certain instances.

Such efforts could not be compared with the success met with by the production of successive charges of *tough arsenical copper* of 25 to 50 tons each, all of the same desirable and consistent quality throughout, as was obtained by present up-to-date practice, and in the writer's opinion it was largely due to that fact that the recognized superiority of *tough arsenical copper* had been so firmly established. It was that quality of copper that was now called for in all important specifications, including the British Engineering Standards Committee, and practically all Railway Companies, shipbuilders, and Government Departments.

Mr. F. JOHNSON wrote, in continuation of his remarks made at the meeting, that he had now had a better opportunity of studying Sir Gerard Muntz's remarks, and of the figures which he had furnished in support thereof. The more he thought of Sir Gerard Muntz's expression of his views concerning the functions of arsenic in copper the more chaotic the whole problem became. If Sir Gerard were right, then those railway and marine engineers who in their hundreds employed arsenical copper in preference to pure copper were wrong. In the same category also were those practical men who, in the various copper-works in this country, could testify to the great value of arsenic in the process of producing "tough" copper. But was it meant by Sir Gerard Muntz that his remarks applied to all classes of copper produced in various ways? The author did not think this was the case ; he rather thought that Sir Gerard referred to only one class of copper, viz., fairly pure copper melted in crucibles and deoxidized with phosphorus. To narrow the question down in this way was to eliminate many otherwise inevitable points of disagreement. It was not surprising that Sir Gerard had discarded

arsenic if he regarded it as a deoxidizer, since he* (the author) and Law † had conclusively shown that arsenic affected the physical condition of cuprous oxide and not its quantity.   Concerning the influence of arsenic on occluded gases, if Sir Gerard meant that arsenic was inferior to phosphorus or silicon, then he (the author) was in complete agreement.   If. however. one considered the influence of arsenic in a big molten charge of " tough " copper, it was a well-understood thing among copper-refiners that arsenical copper showed less tendency to dissolve gases during the poling operation or subsequently than copper free from arsenic.   In such a case the question of deoxidizing did not arise, the arsenic being added, not with the idea of deoxidizing—that was left to the action of carbon and reducing gases—but with the idea of assisting the refiner in his task and of improving the physical and mechanical properties of the metal.   As he had formerly pointed out,‡ the advantages of arsenic were numerous.   To the manufacturer of " tough " copper arsenic was a friend. because it—

1. Lowered the susceptibility of copper for dissolving gases, thus conferring greater soundness and toughness.

2. Neutralised the ill effects of bismuth and lead.

3. Enabled copper to withstand better the harmful effects of overheating.

4. Improved the cold-working properties of copper by reason of its scattering action on the globules of cuprous oxide.§

To the engineer arsenic was a friend because, on account of the foregoing effects, a better material was placed at his service by the manufacturer than would be the case if arsenic were absent.   He (the author) thought that engineers should state their own case, but there were strong indications that arsenical copper was of more value to them than purer copper on account of its retention of mechanically-bestowed hardness at a higher temperature than in the case of the latter.   It had been stated also that arsenical copper was more durable at high temperatures in service and resisted better the action of flame than pure copper.   He (the author) had every reason to believe also that arsenical copper, *ceteris paribus*, had greater resistance to corrosion than pure copper. ¶

The advantages of arsenic to the manufacturer were beyond dispute, but he (the author) thought that in view of Sir Gerard's strong denunciation of it, experimental evidence as to its value or otherwise to the engineer would be very welcome.

Sir Gerard had asked for particulars of the alternating stress tests. He had given these fully in a former paper.‖   The test-pieces were 6 inches by ⅜ inch diameter, and the length of specimen free was, he be-

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* P. 292.

† *Journal of the Institute of Metals*, No. 2, 1912, vol. viii. p. 227.

‡ Paper read before the Birmingham Local Section to the Institute of Metals, No. 2, February 1913, vol. v. p. 78.

§ See Figs. 9 and 10 of present paper.

‖ *Journal of the Institute of Metals*, No. 2, 1910, vol. iv. p. 177.

¶ *Proceedings of the Institution of Civil Engineers*, vol. cliii. (1902–3), pp. 407–408.

lieved, about 4 inches, the amount of movement either side of the vertical being $\frac{3}{8}$ inch, so that, at the level of the slotted arm, the specimen moved through $\frac{3}{4}$ inch at each stroke. He thanked Sir Gerard for his interesting figures. He could add nothing more to what he had already said concerning Sir Gerard's remarks as to being behind the times. If there were sufficient evidence in front of the Publication Committee to convince them that the paper was behind the times, they ought not to allow it to appear in the *Journal*. He was content to leave the matter in their hands.

He could not help thinking that, in view of Sir Gerard's opinions and the vigour with which he had supported them, an exhaustive series of practical tests by engineers of " tough " arsenical furnace-refined copper and of pure deoxidized copper in various forms and in different situations would be exceedingly valuable. If subjected to identical treatment in service, the two classes of copper would then reveal any points of difference as regards suitability and durability.

In reply to the communication, Mr. Johnson wrote that he was at a loss to understand why such stress should be laid upon the past experiences of gentlemen who had been interested in alloys and methods of production similar to those described in the paper. It was of very great interest to him to learn of their experiences, but he claimed that the facts as detailed in the paper had suffered no loss either of usefulness or originality, since not a single case had been quoted of forged arsenical copper deoxidized by the aid of ferro-silicon. Had he (the author) merely claimed that he had discovered how to deoxidize cop per such a claim at the present day would be deserving of ridicule, but to those who took the trouble to read the paper carefully it would be apparent that its originality was perfectly valid.

Mr. Tomlinson's communication was of very great interest, and he (the author) would have been glad had Mr. Tomlinson quoted such facts as could be accepted as indisputable proof of his argument. He appreciated his point regarding the consistent and uniform quality of tough arsenical copper made from large furnace-charges, especially so because of the good turning properties conferred by the small amount of oxide contained in that class of copper. This feature was of great importance when dealing with stay-bolts which had to be turned and screwed in large quantities. He was very glad the paper had roused so much practical interest, and it gave him great pleasure to thank sincerely those gentlemen who had contributed to the discussion.

THE MICRO-CHEMISTRY OF CORROSION.*

Part I.—SOME COPPER-ZINC ALLOYS.

By CECIL H. DESCH, D.Sc., Ph.D., and SAMUEL WHYTE, B.Sc.

(Respectively Graham Young Lecturer and Assistant in Metallurgical
Chemistry in the University of Glasgow).

The object of this investigation is to throw some additional light on the mechanism of the process of corrosion. Owing to the lack of homogeneity of most technical alloys, laboratory experiments fail to give much useful information as to their relative powers of resistance to corrosion, and this problem can only be attacked by carefully-planned experiments on a large scale, such as those undertaken by the Corrosion Committee of this Institute. There remain, however, many subsidiary problems which may with advantage be investigated in the laboratory, using small specimens of alloys prepared from purified materials, and the results of such investigations may pave the way for comparative experiments on a technical scale.

Whilst much work has been done on the chemical mechanism of the corrosion process, and on the electrolytic conditions, it does not appear that other physical factors which are involved have received adequate attention. These factors include the loosening of structure produced by the preferential solution of one micrographic constituent in alloys consisting of more than one solid phase; exfoliation; the formation of protective layers, either of residual metal or of precipitated basic salts or oxides; and the influence of crystalline boundaries in homogeneous alloys.

Experiments bearing on some of these points have been undertaken in this laboratory, attention being directed, after a number of preliminary tests had been made, to certain alloys of copper and zinc.

In alloys of the Muntz metal class, composed of two micro-

* Taken as read at Annual Autumn Meeting, Ghent, August 29, 1913.

graphic constituents, the α and β solid solutions, corrosion undoubtedly begins by the removal of zinc from the β-constituent, the α-crystals only being attacked at a later stage. For this and other reasons, the β solid solution of zinc in copper was first selected for systematic investigation, although alloys containing this constituent alone are not met with in ordinary technical practice. It is true that, as has been proved by the remarkable work of Professor Carpenter, the β-constituent of slowly-cooled alloys is not a homogeneous solid solution, but an ultra-microscopic intermixture of the α and γ phases. This fact, however, has not presented any obstacle. Prolonged annealing does not give rise to any visible segregation in the absence of an excess of the α or γ phase, and it is shown below that alloys quenched respectively above and below the eutectoid point present quantitative differences in the rate of corrosion, but do not differ in regard to the nature of the process.

Reference must be made to the reports of Dr. Bengough to the Corrosion Committee for previous work on this subject, and in this place it will be sufficient to refer to the work of Lincoln and his collaborators.[*] In these experiments, alloys of copper and zinc were corroded in normal solutions of various salts, the loss of weight after a given time being determined, together with the composition of the " corrosion product." The latter included (a) a loose, flocculent precipitate of basic salts ; (b) an adherent deposit of similar character which could be dislodged by rubbing the specimen with a rubber-tipped rod ; (c) a firm, coppery deposit, which could only be removed by means of a knife, and sometimes then only imperfectly. In addition, the " corrosion product " must have included (d) any crystals removed by exfoliation without being dissolved. It is not clear whether the small quantity of metal in solution (e) in the electrolyte was included in the analysis or not. It is thus evident that the product analysed was the sum of several distinct substances, and that any differences between the relative proportions of (a), (b), (c), and (d) in different cases would be obliterated by the experimental method adopted.

* A. T. Lincoln, D. Klein, and P. E. Howe, *Journal of Physical Chemistry*, 1907, vol. xi. p. 501 ; A. T. Lincoln and G. C. Bartells, *ibid.*, 1908, vol. xii. p. 550.

We have found that such differences actually exist, and exert an important influence on the course of corrosion.

In consideration of these, and other results obtained elsewhere, it was decided to adopt the electrolytic method of corrosion, but to distinguish carefully between the products (*a*) to (*c*) above, and to supplement the chemical analyses by a microscopical examination. Objections may be raised to the use of an electric current in bringing about corrosion, on the ground that it does not correspond with the conditions generally met with in practice. A purely chemical method, however, does not appear to be practicable in laboratory experiments on a small scale. Corrosion under such circumstances is extremely slow and subject to irregular and unaccountable variations, whilst accelerated tests, using acid or ammonia, are known to give results which are often misleading. Corrosion with the aid of an applied electromotive force is under complete control and eliminates accidental differences, so that similar conditions may be reproduced time after time with different specimens. In view of the fact that all chemical corrosion is ultimately electrolytic in character, it seems probable that conclusions reached as the result of such experiments may prove useful in the discussion of the conditions of technical practice.

So far, the investigation has been confined to β-alloys of copper and zinc (slowly cooled and also quenched from above the temperature of transformation) and to alloys containing small quantities of tin and iron respectively. Experiments dealing with the influence of lead, aluminium, and nickel are in progress.

EXPERIMENTAL METHOD.

The alloys were prepared from cathode copper and Kahlbaum's zinc, melted and mixed in the usual way in salamander crucibles, using a protecting layer of borax. They were cast in warm iron ingot moulds, after stirring with a carbon rod, and allowed to cool under the layer of borax. The small ingots thus obtained were sawn through and examined microscopically, and a portion taken for analysis. The specimens for the corrosion tests were cut from the ingot transversely,

and reduced in size so as to give one surface exactly 12·5 millimetres square, which was ground on emery-paper in the usual way, finishing with Dujardin's 05 paper. For most of the experiments, polishing was found to be unnecessary, and the surface obtained after grinding on this fine emery was adopted as a standard.

The electrolyte employed throughout was a 5 per cent. solution of sodium chloride, of which 1 cubic centimetre was used for each of the short-period tests, and 100 cubic centimetres for each of the continued tests. In order to carry out an experiment, a specimen prepared as above was placed horizontally with the ground surface uppermost, the lower surface resting on a copper spiral connected with one pole of the battery. A vertical wall of plasticine or paraffin wax was then built up round the specimen, forming a rectangular cell to retain the electrolyte. The specimen was made the anode, the cathode being a loop of platinum wire, placed horizontally just beneath the surface of the liquid. The current was obtained from two dry cells, giving an electromotive force of 3 volts. No gas was given off at the surface of the specimen, and the deposit was therefore not disturbed during its formation. After the lapse of a definite time, usually five minutes, the cathode was removed, the contents of the electrolytic cell washed out into a beaker for analysis, and the wall of plasticine or paraffin wax removed. The solution always contained a flocculent precipitate in suspension. In addition to this, there was frequently, as noted below, a more or less adherent deposit of basic salts on the surface of the metal. This was removed by means of a jet from a wash-bottle and separately analysed. The surface of the metal was then dried and examined microscopically. Finally, the coppery layer was removed for analysis, and the underlying yellow surface exposed for microscopical examination. In most cases, the coppery layer could be loosened at one edge by means of a knife, and peeled off without injury to the specimen, but occasionally rubbing with an edge of soft wood was necessary.

The alloys containing tin and iron respectively were prepared as above, with the addition of the required quantity of Kahlbaum's pure tin or of electrolytic iron prepared by the Langbein-Pfannhauser process.

Analytical Methods.*

Owing to the small scale of the experiments, it was neces-
sary to devise certain modifications of the ordinary analytical
methods for the determination of the composition of the
solutions and precipitates obtained after corrosion.   Under
these conditions, the quantity of each metal to be estimated
in one experiment was to be measured in milligrammes, and
often amounted only to a fraction of a milligramme.   It was
also desirable that the methods employed should be rapid,
and should avoid tedious separations.   After a number of
preliminary tests, the following methods were adopted and
employed throughout :

Copper.—(*a*) In quantities less than 0·1 milligramme.   Addi-
tion of H_2S water to the slightly acid solution, and comparison
with the coloration given by a standard solution of copper.

(*b*) In quantities greater than 0·1 milligramme.   Addition of
ammonia and colorimetric comparison with the standard.

The standard solution is prepared by dissolving electrolytic
copper in nitric acid and evaporating with hydrochloric acid
until nearly all the acid has been expelled.   1 cubic centi-
metre = 0·1 milligramme copper.

If iron be present, the hydroxide must be removed by
filtration before comparing the blue ammoniacal solutions.

Zinc.—(*a*) In quantities less than 0·1 milligramme copper
being present.   The solution is made slightly ammoniacal,
and 1 cubic centimetre of a 10 per cent. solution of potassium
ferrocyanide is added.   The tube is then plunged into hot
water, when the precipitate which is formed at first redissolves,
yielding a solution the colour of which inclines to green with
large proportions of zinc and to red when the copper is in
excess.   The colour is then compared with that of two or
three blanks, containing the same quantity of copper as the
solution under examination (this having been determined
previously), but to which varying quantities of zinc have been
added.   The true proportion of zinc is readily found by
interpolation.   This method has proved to be very satisfactory
in practice.

* These methods were worked out by Mr. Whyte.

The standard solution of zinc is prepared by dissolving pure zinc in hydrochloric acid, and removing the excess of acid by evaporation. 1 cubic centimetre $= 0\cdot1$ milligramme zinc.

(*b*) In quantities greater than $0\cdot1$ milligramme. Copper and tin (if present) are removed by means of hydrogen sulphide, and iron by ammonia. The filtrate is evaporated to dryness and the residue dissolved in a little water : 5 cubic centimetres of concentrated hydrochloric acid are then added, and the hot solution is titrated in the usual manner with a standard solution of potassium ferrocyanide, 1 cubic centimetre of which corresponds with $0\cdot1$ milligramme of zinc. A freshly-prepared solution of uranium acetate is used as the indicator. If the quantity of zinc to be estimated exceeds 2 milligrammes a drop indicator is employed in the usual way, but with smaller quantities of zinc greater accuracy is obtained by adding the indicator to the zinc solution and titrating until a permanent brown coloration appears.

Tin.—Copper and tin are precipitated together as sulphides, and the precipitate is collected on a filter and washed. The two metals are then separated by digestion with a warm solution of sodium hydroxide, and the filtered solution is very slightly acidified with hydrochloric acid. In the comparison tube is a solution of hydrogen sulphide, to which is added, drop by drop, a standard solution of stannous chloride, prepared from pure tin, of which 1 cubic centimetre $= 0\cdot1$ milligramme tin. The yellow colorations are then compared.

Iron.—This is estimated colorimetrically in the usual manner with potassium thiocyanate, the standard solution being one of which 1 cubic centimetre $= 0\cdot1$ milligramme iron.

The smallest quantities which can be determined with accuracy by the above methods are :—

	Milligramme.
Copper (sulphide)	$0\cdot01$
Copper (ammonia)	$0\cdot1$
Zinc (colorimetric)	$0\cdot025$
Zinc (volumetric)	$0\cdot05$
Tin	$0\cdot01$
Iron	$0\cdot005$

Record of Experiments

In the final series of experiments, three alloys were used, one of which was examined in the slowly cooled and also in the quenched condition. The analyses are given in Table I. The analyses were made by the ordinary methods, copper being estimated electrolytically, and also by the iodine method, identical results being obtained. The figures in the last two columns give the composition of the equivalent copper-zinc alloys, determined by Guillet's method,* the coefficients of equivalence of tin and iron being taken as 2 and 0·9 respectively.

Table I.

Alloys.	Copper. Per Cent.	Zinc. Per Cent.	Tin. Per Cent.	Iron. Per Cent.	"Fictitious Values," by Guillet's formula.	
					Copper. Per Cent.	Zinc. Per Cent.
I. and II.	52·95	47·05	...	...	52·95	47·05
III.	53·58	45·26	1·16	...	52·97	47·03
IV.	53·24	45·71	...	1·05	53·25	46·75

The "fictitious values" for zinc and copper represent the composition of the pure copper-zinc alloy which would correspond most closely with the actual ternary alloy. It will be seen that the alloys used are closely comparable from this point of view.

In the first series of experiments, the application of the current was continued for five minutes, the products being analyzed immediately afterwards. Alloys I. and II. contain copper and zinc only, I. being slowly cooled and II. quenched from $750°$ in ice and water, whilst III. and IV. contain added tin and iron respectively. The results of these tests are shown in Tables II., III., and IV. By " precipitate " is meant the flocculent precipitate of basic salts which appears in the electrolyte, and is readily separated from the specimen, whilst " adherent

* L. Guillet, *Revue de Métallurgie*, 1906, vol. iii. p. 243.

TABLE II.—*Composition of Precipitate.*

Alloy	Milligrammes					Per Cent			
	Copper.	Zinc.	Tin.	Iron.	Total.	Copper.	Zinc.	Tin.	Iron.
I.	0·07	2·85	…	…	2·92	2·4	97·6	…	…
	0·07	3·00	…	…	3·67	2·3	97·7	…	…
II.	0·08	2·20	…	…	2·28	3·5	96·5	…	…
	0·065	2·40	0·02	…	2·465	2·6	97·4	…	…
III.	0·10	2·40	0·02	…	3·32	2·71	72·3	0·6	0·8
	0·55	1·80	…	…	2·37	2·33	75·9	0·8	0·8
IV.	0·35	3·45	…	0·03	2·83	9·1	90·1	…	…
	0·35	3·30	…	0·03	3·68	9·5	89·7	…	…

TABLE III.—*Composition of Adherent Layer.*

Alloy	Milligrammes					Per Cent			
	Copper.	Zinc.	Tin.	Iron.	Total.	Copper.	Zinc.	Tin.	Iron.
I.	1·90	0·60	…	…	2·50	76·0	24·0	…	…
	1·90	0·60	…	…	2·50	76·0	24·0	…	…
II.	2·32	0·23	…	…	2·55	91·0	9·0	…	…
	2·05	0·14	0·06	…	2·19	93·6	6·4	…	…
III.	1·40	0·40	0·06	…	1·86	75·3	21·5	3·2	0·7
	2·35	0·21	…	0·01	2·62	89·8	8·0	2·2	0·4
IV.	2·60	0·10	…	0·01	2·71	95·9	3·7	…	…
	2·55	0·05	…	…	2·61	97·7	1·9	…	…

layer" denotes the metallic deposit * which remains attached
to the specimen and is moved by flaking. The number of
milligrammes of each metal in the respective products is
shown, and the results are also expressed in percentages, in
order to bring out more clearly the ratio of copper to zinc,
and the proportion of third metal, if any. Each experiment
was performed in duplicate.

Any metal which remained in solution in the electrolyte
has been included in the precipitate. A few special tests
showed that the quantity was in general very small, and
no useful purpose would have been served by keeping these
two fractions apart. As an example, an analysis of the
electrolyte after a 45-minute test of Alloy I. may be given :—

	Copper. Per Cent.	Zinc. Per Cent.	Total Milligrammes.
In solution	0·01	0·67	0·68
Precipitated	0·75	24·60	25·35

TABLE IV.—*Total Corrosion Product.*

Alloy	I.	.	.	.	5·42 and 5·57	milligrammes
,,	II.	.	.	. 4·83	,, 4·655	,,
,,	III.	.	.	. 5·18	,, 4·99	,,
,,	IV.	.	.	. 6·54	,, 6·29	,,

In the case of Alloy I., a further experiment was performed,
in which, after corroding in the usual manner for five minutes,
the electrolyte was decanted and replaced by fresh solution,
the adherent metallic layer remaining undisturbed. This was
repeated, there being in all six periods of five minutes each.
The results, collected in Table V., show a progressive increase
in the copper content of the precipitate.

On the other hand, when the same electrolyte was allowed
to remain in contact with the specimen, the connection with
the battery being maintained, corrosion soon came to a stand-
still. A new series of experiments was therefore undertaken,
in which the settling of the precipitate of basic salts was

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* In the case of Alloy III. this also contains a small quantity of non-metallic matter.

TABLE V.—*Composition of Precipitate from Alloy I.*

	Milligrammes.			Per Cent.	
	Copper.	Zinc.	Total.	Copper.	Zinc.
1st period . .	0·07	2·85	2·92	2·4	97·6
2nd ,, . .	0·07	2·85	2·92	2·4	97·6
3rd ,, . .	0·15	2·82	2·97	5·1	94·9
4th ,, . .	0·20	2·82	3·02	6·6	93·4
5th ,. . .	0·32	2·72	3·04	10·5	89·5
6th ,, . .	0·50	2·70	3·20	15·6	84·4

prevented, and fresh electrolyte was continually brought into contact with the surface of the alloy. These experiments were conducted in the following manner :—

A vertical wall of plasticine was built up around each specimen as usual, but a lip was formed so as to allow the solution to overflow just above the level of the platinum cathode, the liquid then flowing into a beaker. A burette containing 5 per cent. sodium chloride solution was then placed above the specimen, the liquid falling drop by drop at a constant rate. 100 cubic centimetres of the solution were used in each experiment, the time occupied being in one series 45 minutes, and in another one hour. The flocculent precipitate did not settle, but was continually washed over into the beaker, so that the surface of the specimens remained clean, with the exception of the alloy containing tin, which became coated with a tough, white layer, which exhibited deliquescence when dried and exposed to the air. The adherent metallic layer was peeled off for analysis. The results are collected in Tables VI., VII., and VIII.

The figures in Table VIII. show that the β-alloy quenched above its transformation point is corroded to a greater extent than the alloy which has undergone the normal transformation during cooling, and that, whilst tin greatly retards the corrosion, iron exerts a very conspicuous accelerating influence. These facts are discussed in greater detail below.

Table VI.—*Composition of Precipitate.*

Alloy.	Time. Minutes.	Milligrammes.				Total.	Per Cent.			
		Copper.	Zinc.	Tin.	Iron.		Copper.	Zinc.	Tin.	Iron.
I.	45	0·76	25·27	…	…	26·03	2·9	97·1	…	…
	60	1·20	29·98	…	…	31·18	3·8	96·2	…	…
II.	45	1·10	27·60	…	…	28·70	3·8	96·2	…	…
	60	1·25	32·58	…	…	33·83	3·7	96·3	…	…
III.	45	0·85	12·25	…	…	13·10	6·5	93·5	…	…
	60	3·75	16·00	trace	0·58	19·81	18·8	80·9	trace	2·2
IV.	45	3·25	29·45	0·06	0·98	33·98	9·8	89·0	0·3	1·2
	60	6·00	35·88	…	…	42·56	14·1	84·3	…	…

Table VII.— *Composition of Adherent Layer.*

Alloy.	Time. Minutes.	Milligrammes.				Total.	Per Cent.			
		Copper.	Zinc.	Tin.	Iron.		Copper.	Zinc.	Tin.	Iron.
I.	45	16·00	0·90	…	…	16·90	94·7	5·3	…	…
	60	27·00	0·34	…	…	27·34	98·7	1·3	…	…
II.	45	30·00	0·26	…	…	30·26	99·1	0·9	…	…
	60	36·00	0·14	…	…	36·14	99·6	0·4	…	…
III.	45	14·10	0·30	…	…	14·55	96·9	2·1	…	…
	60	17·50	0·83	0·15	0·025	18·51	94·5	4·5	1·0	0·1
IV.	45	22·00	0·15	0·18	0·035	22·75	99·2	0·7	1·0	0·1
	60	28·00	0·27	…	…	28·365	99·2	0·7	…	…

TABLE VIII.—*Total Weight of Corrosion Product.*

Alloys.				Milligrammes.	
				45 Minutes.	60 Minutes.
I.	.	.	.	42·93	58·52
II.	.	.	.	58·96	69·97
III.	.	.	.	27·65	38·32
IV.	.	.	.	55·25	80·86

MICROSCOPICAL OBSERVATIONS.

The alloys were found to present marked differences in regard to the alteration of appearance during corrosion. The

FIG. 1.—Alloy IV. 5-minute Test. Adherent Copper Layer.
Magnified 90 diameters.

adherent layer had the appearance of copper (except in the case of Alloy III., containing tin, which became coated with a white deposit, below which was the usual coppery layer). On detaching this layer and peeling, the crystalline structure of
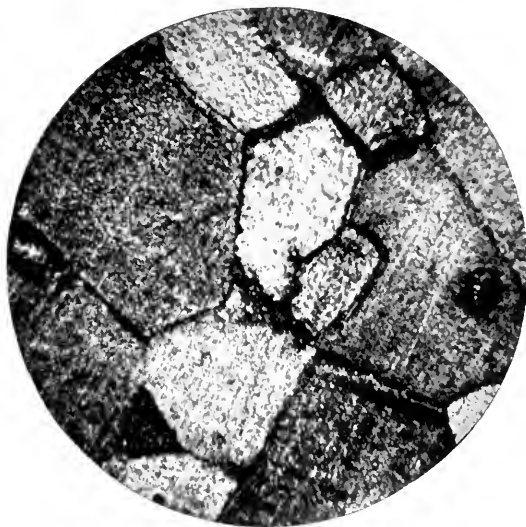
FIG. 2.—Alloy IV. 5-minute Test. Copper Layer Removed.
Magnified 90 diameters.

FIG. 3.—Alloy IV. 1-hour Test. Adherent Copper Layer.
Magnified 36 diameters.

the alloy was generally clearly visible, and there was no con-
tinuity between the adherent layer, composed almost entirely
of copper, and the unchanged alloy beneath. The only ex-
ception to this rule was observed after very prolonged etching,
when the borders of the crystals were found to be affected as
described below.

The surface of the coppery layer shows, more or less dis-
tinctly, the outlines of the β-crystals from which it is derived.
This effect is seen in Fig. 1, which may be compared with
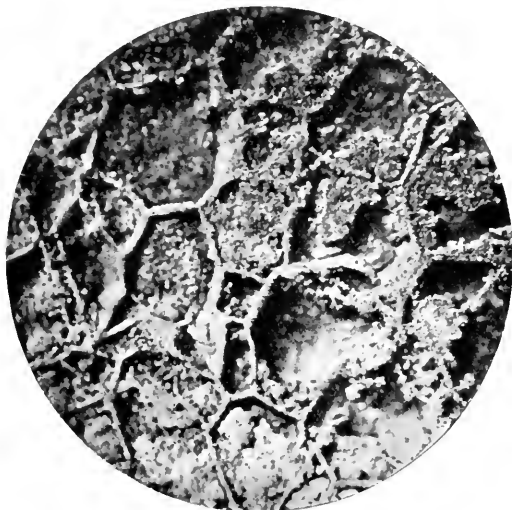
Fig. 4.—Alloy IV. 1-hour Test. Adherent Copper Layer.
Magnified 36 diameters.

Fig. 2, representing a neighbouring area on the same speci-
men, after the copper had been detached. After the long
period corrosion tests, the edges of the β-crystals could some-
times be seen in relief. This was especially the case with
Alloy IV., containing iron, the copper-covered surface of which
is seen in Figs. 3 and 4. In the latter figure, the boundaries
form cellular walls in high relief. After stripping off the
copper, the crystals were found to have been very unequally
attacked, as is shown in Fig. 5. The white areas in the
photograph represent clean, glistening areas of the β-alloy,

Fig. 5.—Alloy IV. 45-minute Test. Copper Layer Removed.
Magnified 65 diameters.

FIG. 6.—Alloy I. 5-minute Test. Copper Layer Removed.
Magnified 18 diameters.

whilst the darker areas are considerably depressed below the surrounding surface, and more or less coloured by adhering films of copper, which were not readily removed from these areas.

The readiness with which the film of copper may be detached is worthy of remark. The removal of zinc necessarily commences at the surface and proceeds downwards into the alloy. It might perhaps be expected that the proportion of zinc would diminish downwards in a continuous manner.

FIG. 7.—Alloy I. 1-hour Test. Deeply Etched Surface beneath Copper Layer.
Magnified 18 diameters.

This is not the case in any of the alloys that we have examined. The removal of zinc is practically complete as far as the action penetrates, and there is no zone of intermediate composition uniting the copper and the unchanged alloy. In experiments shortly to be published by one of us, it is shown that a sharp boundary is characteristic of the diffusion process in solid solutions when accompanied by a chemical reaction, and the present results show that " dezincification," as it is commonly called, proceeds exactly in the manner of a diffusion process.
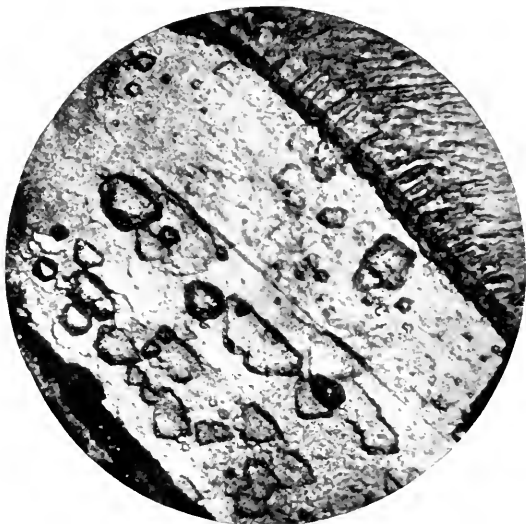
Fig. 8.—Alloy I. 1-hour Test. Etch-figures due
to Corrosion.
Magnified 90 diameters.
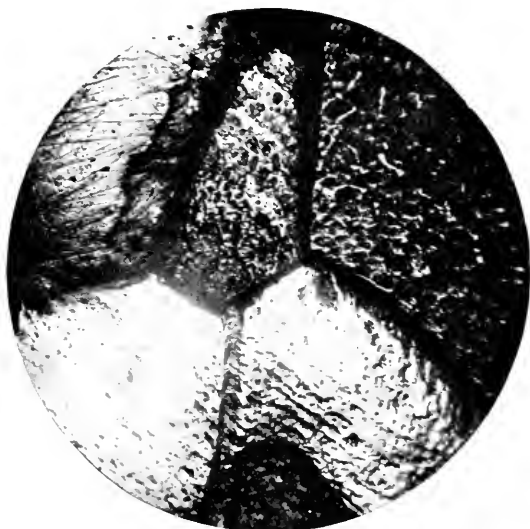
Fig. 9.—Alloy II. 45-minute Test. Copper Layer Removed.
Magnified 65 diameters.

As the action proceeds, the crystalline structure of the alloy is laid bare. This is best seen in the Alloy I., composed of copper and zinc alone. Fig. 6 shows this alloy after corrosion for five minutes. The β-crystals are exposed in the same manner as after etching with ammonia or ferric chloride, differences of orientation giving rise to contrasts in the photograph. After longer corrosion, the inequalities of level are

Fig. 10.—Alloy I. Prolonged Corrosion. Surface Layer Removed by Grinding and Polishing. Copper Boundaries to β-crystals.

Magnified 36 diameters.

much increased, and the surfaces and edges of the β-crystals become deeply scored with etch–figures, usually arranged in parallel lines. The general effect is seen in Fig. 7, although much detail is lost in the photograph, owing to the varying inclination of the etched surfaces to the incident light. Details of the etching are shown under a higher magnification in Fig. 8. Alloy I. was found to give the most regular etch-figures, the more usual effect being that shown in Fig. 9, which is taken from the quenched Alloy II. Alloy III., con-

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taining tin, gave very irregular etching effects, without any clear development of the crystalline structure.

There are several indications that corrosion begins at the boundaries of the crystal grains. On allowing the specimen to remain connected with the battery for several hours, and afterwards grinding away the surface layer and polishing, the crystals could sometimes be seen to be bordered by a distinct layer of copper. This effect is seen in Fig. 10, where, however, the border is somewhat faint owing to lack of contrast. The copper border is sharply separated from the surrounding alloy. In the early stages it is perfectly symmetrical, the bounding surfaces of the two neighbouring crystal grains being affected to an equal degree, but as corrosion proceeds this cannot continue to be the case, in view of the very unequal attack on different crystals as shown in Fig. 7. This point is under investigation.

DISCUSSION OF THE RESULTS.

The figures given above emphasize the importance, in experiments dealing with corrosion, of distinguishing between material which is actually dissolved (here included in the precipitate) and that which remains as a dezincified layer, which may afterwards become mechanically detached. In the absence of mechanical disturbance, this layer may serve as a protection against further corrosion, but if agitated, the layer may scale off from time to time, exposing a fresh surface to the action of the corroding agent.

The removal of zinc from this surface layer proceeds until practically only copper remains. Up to 99·6 per cent. of copper has been found, and it is probable that a part even of the small remaining amount of zinc is mechanically retained by the somewhat porous copper.

As regards the differences between the four alloys under examination, it appears that the effect of quenching from above the transformation temperature increases the tendency to corrosion. This is not evident from the 5-minute tests, and in fact during the prolonged tests it was observed that corrosion set in somewhat more slowly with Alloy II. than with

I., but the difference is very apparent in the 45 and 60-minute test, and was quite distinct in some tests, not included in the tables, lasting for 10 and 15 minutes respectively. As the quenched alloy is in a metastable condition, it should have a greater tendency to dissolve than the stable alloy. The greater initial velocity of solution of the latter may be due to the formation of minute local couples owing to the presence of the a and γ phases in ultramicroscopic subdivision.

There is no evidence that Alloy III., containing tin, has less initial tendency to corrode than the pure copper-zinc alloy. The well-known protective influence of tin must be otherwise explained. We believe it to be mainly mechanical, and due to the formation of a peculiarly tough and adherent deposit of basic salt, in the present instance of oxychloride. This deposit behaves as a protective paint, and exerts a mechanical, and not a chemical, resistance to the further progress of corrosion. The presence of iron, as is shown by the results from Alloy IV., greatly accelerates corrosion, a conclusion which is in accord with practical experience. A few preliminary experiments with a-alloys show that their behaviour is qualitatively similar.

We do not propose at this stage to draw any conclusions as to the behaviour of alloys under technical conditions. We are extending the investigation, and trust that the information accumulated may be of some use in elucidating the mechanism of this very important process.

COMMUNICATIONS.

Dr. G. D. Bengough, M.A. (Liverpool), wrote that he had been much interested in the paper, and had regretted the absence of Dr. Desch from the Ghent Meeting. He thought that a comparison between the course of ordinary chemical corrosion and that of electrically stimulated corrosion was a matter of importance both from a scientific and a practical point of view. He naturally regretted that the authors had selected alloys of the β brass type for their first investigation, as his own experience was confined almost entirely to alloys of the α type ; he looked forward eagerly to the work on this type of brass foreshadowed by the authors ; until this was available, a strict comparison between the two sets of results was not possible.

At the same time he thought that there was some evidence to show that the course of electrically stimulated corrosion was very different from that of ordinary corrosion. In the case of Muntz metal, for instance, he found that the dezincified area which caused such trouble in practice was not coincident with β crystals, but extended over groups of α and β crystals. There might be some slight amount of electro-chemical action initially between the two phases, but it was quickly stopped by the formation of oxide. He was inclined to think that the presence of the layer of oxide (which was formed during the slow process of chemical corrosion, but not, apparently, during the rapid progress of electrically stimulated corrosion) constituted an important difference between the two types of corrosion.

He was, therefore, not quite in accordance with all the remarks on p. 306 of the paper. He considered that it was advisable to distinguish clearly between the two types of corrosion, particularly from the practical, as apart from the strictly scientific point of view. As a consequence, he did not like the title of the paper, and would have preferred to call it the " Microchemistry of electrically-stimulated corrosion." Although all corrosion might be ultimately electrolytic in character, yet the secondary reactions at the ordinary temperature became so important in unstimulated corrosion as to render necessary a clear distinction between the two, at least from a practical point of view.

The results of the authors' experiments appeared to correspond more closely with those carried out at $40°$ C. on Muntz metal than with any of the others described in the Second Report to the Corrosion Committee. In these dezincification of both β and α crystals was observed, and the oxide layer was of less importance than in the experiments carried out at the ordinary temperature. He would like to ask the author if the flocculent precipitates formed in their experiments was white in colour, and consisted almost entirely of zinc oxychloride ; he concluded from the analyses on p. 312 that this was so, and in this case the results for Muntz Metal at $40°$ C. resembled those for the author's β alloy, except that the proportion of zinc in solution was much smaller in the case of the authors' β alloy. In α alloys the amount of zinc

remaining in the solution was approximately the same as that which was precipitated. The greater liability of Muntz metal to dezincification could, perhaps, be correlated with the greater proportion of zinc precipitated as basic chloride, especially if this substance stimulated corrosion as had been suggested in the Report.

The remarkable phenomenon of the removal of zinc approximately completely down to a certain depth beneath which dezincification stops abruptly, leaving an easily detachable layer or plug of copper, had occurred in his own experiments as well as in the authors', and was well worthy of record. He was interested in the paper on the subject foreshadowed by Dr. Desch on p. 319. He was much interested in the analytical methods given on pp. 308 and 309, and particularly in that given for the estimation of minute quantities of zinc on p. 308, which was quite novel to him. He was surprised that the ferrocyanide estimation described on p. 309 had given such good results when used for such small quantities of zinc; he should himself have used the phosphate gravimetric method, which had the drawback of taking a much longer time to carry out.

He was not altogether satisfied with the authors' explanation of the action of tin in retarding corrosion; at any rate it would not entirely cover the facts of the ordinary corrosion on any a alloys. If it acted as suggested it should retard general corrosion at the ordinary temperature, but this it did not do. Its action was to retard dezincification at elevated temperatures. It might, of course, happen that the correct type of protective basic salt was only formed at temperatures higher than the ordinary, and this suggestion might be worth investigation.

He hoped the authors would keep their promise to extend their work to a alloys, and so add to the small amount of skilful and careful work to be found on the subject of corrosion of non-ferrous alloys.

Mr. H. GARLAND (Cairo), wrote to ask if the authors, during their experiments, had formed any opinion as to how the size of the crystal grains affected corrosion? For instance, in the quenched Alloy II. the grains were much smaller than those of Alloy I. The micrographs showed this, and the extra amount of corrosion on Alloy II. might be partially due to the increase in the boundaries, as well as to metastability, as stated by the authors.

Also, could the authors say anything about the influence upon corrosion of incomplete homogeneity in solid solutions?

Presumably, under the conditions of casting, as described in the paper, their Alloy IV. would not be absolutely homogeneous, seeing that it was not annealed.

In deeply-etched specimens of antique copper containing small quantities of iron, the writer had observed very similar characteristics to the cellular formation with the boundaries in relief, shown in Fig. 4, p. 317, and he had attributed it to incomplete diffusion.

With reference to the remark on p. 322, that there were indications

that corrosion began at the boundaries of the crystal grains, the writer sent a micrograph (see below) of a section of an antique copper nail much corroded. It would be observed that the corrosion (black lines and patches) proceeded towards the interior by traversing the granular boundaries, and not by first wholly oxidizing the outer grains and then consecutively converting the inner ones. This explained how the general shape of metal antiquities was often left more or less intact, even in cases where the presence of a thick crust of carbonates and chlorides would at

Edge →

Micrograph of Antique Copper Nail—taken near Edge.
Magnified 75 diameters.

The mottled portion on left of the sharply defined metallic
edge is the section of the green carbonaceous coating.

first lead one to suppose that the external configuration of the article beneath it must certainly have disappeared.

This intergranular progression of corrosion might have some bearing upon the " amorphous cement " theory : the writer had generally found it in old specimens of metals and homogeneous alloys (*i.e.* comparatively pure metals and annealed a solid solutions), though, of course, the samples examined were far from being pure. The effects with " cast-cored " solid solutions he had found to be somewhat different, as described in the second part of his paper contained in this volume of the *Journal.*

The AUTHORS wrote that they had read Dr. Bengough's remarks with great interest. In view of the facts mentioned in the valuable Report to the Corrosion Committee they were inclined to regret that they had not completed their work on α-alloys before proceeding with the β-series. The work had been begun with alloys of the Muntz metal type, but, finding that corrosion always started in the β-areas, they had decided to investigate this series first, then to proceed to the α alloys, and lastly to the alloys containing both α and β-constituents. This work was now proceeding, and it was hoped to communicate a further series of results at the spring meeting. The apparatus had now been improved, so as to give a higher degree of accuracy.

Dr. Bengough's observations with dezincified Muntz metal were not regarded by the authors as being inconsistent with their conclusions. Their method was specially suited to the examination of the initial stages of corrosion, and, in the two-phase alloys, they were of opinion that de-zincification always began in the β-areas, and only after it had proceeded to a certain depth, and the electrolytic potentials at the surface had undergone a corresponding rearrangement, were the α-areas attacked. In deeply-corroded specimens both solid solutions were generally found to be dezincified, although the action proceeded very unequally in the two constituents. They regarded the formation of oxide as being always a secondary phenomenon, occurring after dezincification had gone so far that a spongy, readily oxidizable residue of copper (which might form only a thin layer) was left. With slow corrosion, dezincification and oxidation might keep pace with one another, but with rapid corrosion, as in the authors' experiments, a layer of unoxidized metallic copper would remain. They were, of course, in complete agreement with Dr. Bengough that such secondary reactions might have an important influence on the course of corrosion in actual practice.

In reply to two questions put by Dr. Bengough, the flocculent precipitate observed in their experiments was always white at first, but became more and more green as corrosion continued, owing to the presence of an increasing proportion of copper chloride. Also the methods of analysis described had proved quite satisfactory. They preferred volumetric to gravimetric methods in all cases where the quantities to be estimated were so small.

They agreed that the behaviour of tin in β-alloys could not be employed to explain its action in α-alloys, in view of the difference of its electro-chemical condition in the two cases, and they would not venture to express any general opinion on the influence of tin until further experimental material was available. Alloys containing lead were now under investigation.

In reply to Mr. Garland, the authors were examining the influence of grain size on corrosion. They did not consider that the difference between alloys I and II was to be attributed merely to this cause. The question of imperfect homogeneity did not arise in dealing with β-alloys, which did not exhibit cored structure, but it was, of course, very important in connection with α-alloys, in which the core and periphery of a crystal

might differ very considerably in composition. They were interested in Mr. Garland's observation that corrosion of ancient metals proceeded along crystal boundaries. This was in accordance with their own experiments, and with well-known facts in mineralogy, the alteration of minerals always proceeding along crystal boundaries, and only subsequently extending to the interior of the crystal grains.

METALLOGRAPHICAL RESEARCHES ON
EGYPTIAN METAL ANTIQUITIES.*

By H. GARLAND, F.C.S.

PART I.

It occurred to the author some time ago in connection with the study of the physical changes in metals and alloys due only to atmospheric temperatures that the microscopic examination of metal objects made by the ancient Egyptians in the earliest times should be of considerable value. These metal objects may be divided into two classes, *i.e.* those of a useful character, such as tools, and those of a purely ornamental nature. The latter class includes statues and symbolic articles, but these, being almost without exception extremely impure, were useless for the purpose of this investigation. Tools, however, were much more carefully made, and the Egyptians were fairly successful in keeping the deleterious impurities within low limits, though the analyses appearing in this paper will show that their alloys and metals will not bear comparison with our present-day standards.

A little difficulty was experienced at first in obtaining suitable specimens, the general opinion being that it is almost sacrilegious to cut up these antiquities, but the author eventually succeeded in obtaining a sufficient number for his purpose, and his thanks are especially due to Captains R. G. and T. G. Anderson, both of whom are keen and experienced collectors. He is also indebted to Sir Gaston Maspero, Director of the Egyptian Antiquities Department, for some specimens.

As to the authenticity of the articles it can be safely said there is no doubt, and though the actual period of origin cannot be assigned to several of them, they are all, with the exception of the Roman coin, certainly more than 2000 years old.

There has not been overlooked the possibility of articles of this nature having been at some time previous to their discovery subjected to heat by such means as conflagrations of

* Taken as read at Annual Autumn Meeting, Ghent, August 29, 1913.

cities and so on, and the author therefore has rejected all
specimens that showed any evidence, external or internal (such
as coarse crystallization, &c.), of having undergone any process
of this nature. On the other hand, it was quite easy to detect
a piece of cast or cold worked metal which had never been
through any serious heat treatment, accidentally or otherwise,
since its manufacture.

The metals and alloys dealt with in this paper are bronzes
and impure copper, all of which may be regarded as solid
solutions. The author would ask his readers to keep in mind
the following changes which have been suggested at different
times by several writers as taking place in metals and alloys
at atmospheric temperatures provided a sufficient length of
time is allowed :

    1. Recrystallization after cold work.

    2. Diffusion.

    3. Growth of the crystal grains.

From the photographic evidence produced the expert metal-
lurgists of this Institute will be able to draw their own
conclusions as to how far the above three theories have
foundation in fact and how far they are interdependent, and
they will not be influenced by any of the author's deductions.

FIG. 1.—Photograph of Early Egyptian Copper Knife.

The first specimen is an old copper knife attributed to the
XVIIIth dynasty, and therefore about 3500 years old. It was
of quite an ordinary shape, as will be seen from the photograph
(Fig. 1), and was in a splendid state of preservation. Mr. W. B.
Pollard, B.A., kindly analyzed it with the following result:—

	Per Cent.
Lead	0·63
Iron	1·18
Bismuth	0·44
Tin	0·03
Nickel } Cobalt }	0·26
Arsenic	0·81

The oxygen, as shown by the presence of globules of oxide seen under the microscope, was rather considerable, but it was not estimated.

Neglecting the bismuth, the composition of this knife was regarded as an a solid solution. Photomicrographs of its structure have already appeared in the *Journal*,* but Fig. 2 is a view of the cores at a higher magnification. They are very distinct, and add further proof to the theory of the persistence of the " cast cored " structure, as enunciated by Mr. O. F. Hudson, M.Sc.,† in his paper on " The Microstructure of German

FIG. 2.—Structure of Copper Knife showing Cores.
Vertical illumination.   Etched with 10 per cent. ammonium persulphate.
Magnified 75 diameters.

Silver," read at the 1913 Spring Meeting. These particular cores have endured 3500 years, and appear therefore to be perfectly stable at atmospheric temperatures.

A close microscopic examination of this knife showed that there was a difference in hardness between the cores and the matrix, but it was not readily perceptible before etching. At one time the author had reason to doubt whether the structure was really a " cored " one, or whether the more or less parallel light and dark markings were furrows produced by the emery and eventually revealed by the etching reagent. That they really were " cores " was, of course, proved indisputably by

* *Journal of the Institute of Metals*, No. 1, 1913, vol. ix. p. 118.
† *Ibid.*, pp. 109-112.

their disappearance on annealing, and also by the chemical analysis made subsequently.

The author, therefore, holds that the knife was hammered into shape cold from a cast rod of impure copper having a structure something similar to that shown in Fig. 16, Plate IX., of the paper by Mr. F. Johnson, M.Sc.,* on " The Effect of Silver, Bismuth, and Aluminium upon the Mechanical Properties of Tough-Pitch Copper containing Arsenic."   Further circumstantial evidence that the knife would be hammered cold is afforded by the fact that by this means would the best cutting edge be obtained.

FIG. 3.—Structure of Copper Knife after Annealing.
Vertical illumination.   Etched with 10 per cent. ammonium persulphate.
Magnified 75 diameters.

On examining the structure at a higher magnification it was found that the whole surface was covered by small crystals, barely perceptible at a magnification of 150.   In a previous volume of the *Journal* † is a micrograph of the structure at 270 magnifications.   The grains are very small, and would appear to have suffered no growth in spite of the ages they have had for the process.

On heating the metal, the " cores " disappeared.   The micrograph in Fig. 3 was taken after thoroughly annealing ; there are no " cores," and the grains have grown in a normal manner.

* *Journal of the Institute of Metals*, No. 2, 1910, vol. iv. p. 192.
† *Ibid.*, No. 1, 1913, vol. ix. p. 118.

There seems to be no doubt whatever that the knife had never been through any heat treatment at a temperature high enough thoroughly to anneal it, though of course we cannot say that the recrystallization was not due to work being done on it at a slightly elevated temperature. No appreciable diffusion or crystal growth has taken place during its lifetime.

The next specimen examined was a small bronze chisel about three inches long, of a normal shape, such as possibly a jeweller would use in those days. It cannot be dated

FIG. 4.—Structure of Old Bronze Chisel.
Vertical illumination. Etched with 10 per cent. ammonium persulphate.
Magnified 120 diameters.

exactly, but there is no doubt as to its antiquity, and its age was at least 2000 years.

The " cores " showed especially well because the chisel was only hammered at the cutting edge, and the original structure had not been seriously damaged in the section taken for the micrograph given in Fig. 4. On examination with a higher power it was found that the dark cores had recrystallized, and a close inspection of the micrograph will show indications of it. The tin-rich matrix had, however, undergone no structural change. On thoroughly annealing the specimen, the cores disappeared and the surface became wholly crystalline with some twinning.

Further examples of the persistence of the "cast cored" structure in antique alloys are shown in the succeeding photographs. Fig. 5 is a section of an impure copper arrow tip. In this case the cores have been flattened out by the cold hammering during manufacture. This specimen was also entirely crystalline when examined under a higher power. Upon annealing the "cores" disappeared, and the surface became very similar to that of the copper knife in Fig. 3.

In Dr. Rose's paper on "The Annealing of Coinage Alloys," * he stated that he thought old coins were struck hot, and that therefore they were useless for the study of any recrystalliza-

FIG. 5.—Structure of Copper Arrow Tip.
Magnified 36 diameters.

FIG. 6.—Structure of Roman Coin.
Magnified 120 diameters.

Vertical illumination.   Etched with 10 per cent. ammonium persulphate.

tion or crystal growth which might be due to age alone. In Fig. 6 is reproduced a photograph showing the structure of a Roman coin belonging to the reign of Constantine, and which is therefore about 1600 years old. This coin may have been struck hot, but not hot enough to promote diffusion, as the cores are still in evidence. In the dark parts of the structure some recrystallization was found to have taken place, and there were a few twins, but the matrix had not broken up into grains. This, it will be observed, is the same effect as was found in the bronze chisel previously mentioned.

* *Journal of the Institute of Metals*, No. 2, 1912, vol. viii. pp. 86–114.

Mr. Pollard's analysis is as follows :—

									Per Cent.
Tin .	.	.	.	.	.	.	.	.	0·8
Iron .	.	.	.	.	.	.	.	.	0·65
Nickel	.	.	.	.	.	.	.	.	0·65
Arsenic	.	.	.	.	.	.	.	.	0·09
Silver	.	·	.	.	.	.	.	.	1·71

Traces of Gold, Zinc, Cobalt, Lead, and Bismuth.

A perfectly homogeneous structure on annealing was not to be expected from such an alloy, but the " cores " disappeared and the surface became crystalline with twin markings and a slight amount of eutectic in places.

FIG. 7.—Structure of Bronze Spatula.
Vertical illumination. Etched with 10 per cent. ammonium persulphate.
Magnified 120 diameters.

In considering a slightly different aspect of ageing, it is well known that when a metal or solid solution is hammered cold the crystal grains are distorted and broken up, and a section of such a metal shows a multitude of lines. Fig. 7 demonstrates the stability of this structure at ordinary tem-peratures.

The author was fortunate enough to obtain an ancient Egyp-tian spatula made from a bronze rod which had been annealed prior to being hammered into shape in the cold state, and had not been subjected to any heat treatment subsequently. It was shaped in the form of a circular rod 0·1 inch in diameter, about $3\frac{1}{2}$ inches long, flattened out at one end. A transverse section was cut through the rod, and Fig. 7 shows the confused

structure due to the original hammering.   The metal had not recrystallized after the cold work, but was apparently in the same state as when it left the makers' hands.   It would seem that after being partially worked the spatula was annealed, and that after further severe cold working it was not subjected to a second heat treatment.   It is rather remarkable that the flow lines have been preserved to the present day, and that if the internal strains have been relieved by an ageing effect (which seems doubtful) these lines did not disappear at the same time.

On annealing at a low temperature the alloy recrystallized
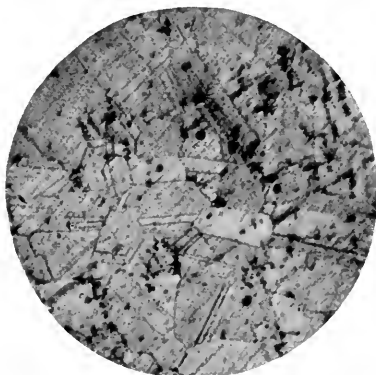
FIG. 8.—Structure of Bronze Spatula after Annealing.
Vertical illumination.   Etched with 10 per cent. ammonium persulphate.
Magnified 120 diameters.

into a fine type of crystal grains, which, on increasing the temperature, grew in the usual manner.   The micrograph in Fig. 8 was taken after thorough annealing in order to get as good a photograph as possible at a medium magnification so as to be within the limits of photography as practised in the tropics.

It would, of course, not be safe to say that such recrystallization as was found to have occurred in the specimens mentioned in this paper was due solely to age, but of many specimens examined by the author not one has been noted which had not recrystallized in some part of its structure, usually in the copper-rich part.   Further, in the majority of samples the size of the crystal grains was of a very fine order.

From the results of these investigations the author considers
that the structural changes that take place in such metals and
alloys at atmospheric temperatures—in the absence of mechani-
cal effects, such as vibration and so on—are trifling.   It seems
that to promote diffusion in a solid solution, or to increase the
size of the crystal grains, a more or less elevated temperature
is a *sine quâ non*.

PART II.*

SINCE the first part of this paper was prepared, a most in-
teresting antique specimen has come into the author's hands,
and as it has some bearing upon the general question of
corrosion, a special effort has been made to frame the following
description of it for inclusion in this volume of the *Journal*.

It is believed by the author to be part of a copper dagger
which was originally contained in a sheath of the same metal,
but the latter, being very thin, had entirely oxidized.   The
archæological authorities give its period as the First Dynasty,
and therefore some seven thousand years have elapsed since
it was first made.

The following is the analysis of the metal, omitting
oxygen :—

		Per Cent.
Arsenic	.	0·39
Lead .	.	trace
Iron .	.	0·08
Copper (by difference)	.	99·53
Bismuth, Tin, Nickel	.	Nil

Owing to the entire oxidation of the sheath, there was a
crust of green copper carbonate, &c., about ¼-inch thick sur-
rounding the metal core of the dagger itself, which was in a sur-
prisingly good state of preservation.   In the space between the
dagger and its sheath, on each side, the corrosion had been able
to proceed in a more uniform and undisturbed manner than
generally happened with those old metal articles, and it was
possible, upon removing the crust, to distinguish on the
surface of the dagger the forms of crystallites in sunk-relief,

* Not presented at Ghent with the foregoing.—ED.

Y

due to their having corroded more rapidly than their arsenic-rich boundaries. The specimen was therefore at once recognized as being still in its original " cast-cored " state, and the interesting feature was photographed. Fig. 1 is a micrograph of the external surface : the light markings, the shapes of which, though somewhat irregular, are readily identified with crystallite formation, are the depressions left by the corroded copper-iron rich crystallites, but they were allowed to remain filled up with green cupric carbonate in order to afford some contrast for photographic purposes.   Other
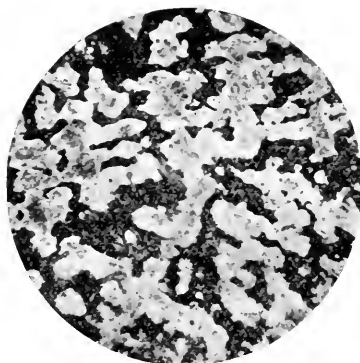
Fig. 1.—View of Surface of Copper Dagger, showing Selective Corrosion. Light parts are depressions left by corroded crystallites filled up with cupric carbonate. Magnified 30 diameters.
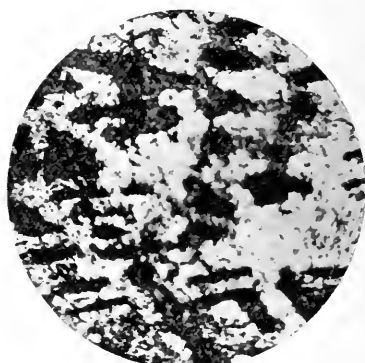
Fig. 2.—Section showing Internal Selective Corrosion near Surface. Dark parts are corroded copper-rich crystallites. Slightly etched. 10 per cent. ammonia persulphate. Magnified 50 diameters.

parts of the surface, where the carbonate had been wholly removed, showed more perfect crystallite figures, but they were not so suitable for photographing.

The forms of the crystallites could also be seen in relief upon the pieces of carbonaceous crust removed from the specimen.

This selective oxidation was also detected in the interior of the metal. Near the edges of the section microscopic examination showed that the crystallites had entirely corroded, though their contours were not so well defined as the external ones. Figure 2 is a section, the dark parts of which are the corroded crystallites.

This dagger had apparently been made in the same way as the knife described in Part I., but as some parts of the section near the edges showed a little twinning, perhaps a slight amount of hot work had also been done on it. That it had never been properly annealed, and that no appreciable diffusion had occurred during its lifetime, was abundantly clear when the examination had proceeded only so far, but on etching the section the " cores " came out with distinctness, as shown in Fig. 3. This micrograph should be compared with that of a somewhat similar alloy prepared by Mr. F. Johnson, and

FIG. 3.—Showing " Cores." Etched, 10 per cent. ammonia persulphate. Magnified 50 diameters.

FIG. 4. — Showing general arrangement of Recrystallization. Etched, chromic acid. Magnified 65 diameters.

referred to on p. 278. The structure of that alloy consisted similarly of " cores " with the oxide globules chiefly strung along the light-coloured arsenic-rich parts.

The author would remark that he finds ammonium persulphate by far the best etching medium for revealing " cores "; ammonia is much less effective. For giving acute definition to the crystal boundaries he uses chromic acid, which has proved better than either of the two first-named reagents for this purpose.

The " cores " may be detected to some extent on the simply polished surface, because of the wearing away of the softer phases, but owing to the selective action of ammonium persulphate, which, on repeated applications, eats away the copper-rich crystallites, they are brought to view by the

undulations thus made in a much clearer manner than that given by the slight oxidation films produced by other reagents. A very good way to observe the " cored " structure is to throw the microscope slightly out of focus.

Close examination of the etched section showed that recrystallization had taken place in a somewhat peculiar manner ; there were indications that the actual recrystallization had only affected one part of the structure—the arsenic-rich parts— which had taken the form of attenuated crystal grains following the meanders of this particular phase, thus leaving the other parts (copper-rich) in the form of islands of varying
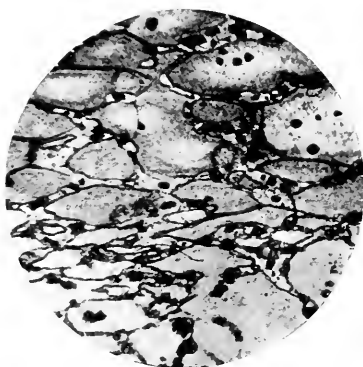
Fig. 5.—Showing how Recrystallization was confined to Arsenic-rich Boundaries. Etched, chromic acid. Magnified 100 diameters.
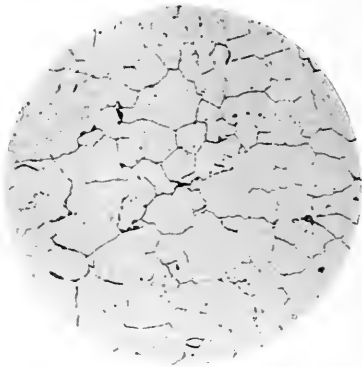
Fig. 6.—After Annealing. Etched, chromic acid, then slightly polished. Magnified 65 diameters.

sizes. This can be seen in Fig. 4, and more clearly at a higher magnification, in Fig. 5.

It may be pointed out that, as is seen in Mr. Johnson's micrograph alluded to above, the metal of the dagger in its original cast state would not show these clear crystal boundaries. There is a possibility, however, that they were induced by the very slight amount of hot work which appears to have been done on the dagger. The author, however, rejects this idea, because, except near the edges of the specimen, as stated, the crystal grains bear no resemblance to the type produced on such alloys by hot work or by annealing cold-worked samples, but are more like the primitive " cast " type of grain.

Moreover, hot work or annealing would have produced re-crystallization in the copper-rich islands. He prefers not to venture any opinion as to whether the recrystallization was brought about in relief of the internal strains set up by the cold hammering, or whether it was induced either by the highly crystalline properties of arsenic or by the presence of the cuprous oxide globules.

Annealing the metal produced the usual results. Fig. 6 shows how the grains assumed a more regular form, and how the oxide migrated to the granular boundaries. The " cores " disappeared. This micrograph was produced by etching with chromic acid, and afterwards lightly polishing ; but, of course, before the latter was done, it was well observed that " cores " were absent. The polishing has obliterated the boundaries here and there. Striations due to polishing scratches appear on this and other photographs not of deeply-etched speci-mens ; they do not, however, interfere with the structure, but the author would say, in explanation, that in common with other residents in Egypt, he has not yet succeeded in keeping out the sand and dust which finds its way into all rooms and receptacles not absolutely hermetical.

In conclusion, the writer wishes to express his indebtedness to Mr. S. H. Trimen for the opportunity of examining this unique specimen, and to Mr. A. Lucas, F.I.C., for kindly allowing the analysis to be made in the laboratory which he so ably directs.

COMMUNICATIONS.

Mr. F. Johnson, M.Sc. (Birmingham), wrote that he was much interested in the composition of the old copper knife, as given on p. 330. The amount of bismuth (0·44 per cent.) was exceedingly high, and he doubted very much if material of the composition stated could survive many blows of the hammer. As the micrographs almost conclusively proved that the knife had been really subjected to "work" (whether entirely cold work could not with certainty be accepted from the evidence adduced), he would suggest that the analytical figures be checked.

The whole subject of the microstructure of ancient tools and other articles was so fascinating, that he hoped Mr. Garland would continue his researches, and throw further light on the methods of production of copper and its alloys, as practised by the ancients.

Dr. T. K. Rose wrote that the author's interesting work went to prove that recrystallization of impure copper, in the sense of the breaking-up of the original crystals distorted by cold work, with the formation of small crystals, took place in course of time at atmospheric temperature, but that the growth of crystals occurred only at higher temperatures. That supported the general views which the writer had been led to form.

Mr. Garland said, on p. 335, that "when a metal or solid solution is hammered cold, the crystal grains are distorted and broken up." The writer would be glad to have references to the evidence on that point, as he could find no traces of the breaking-up of crystals when gold was worked cold, whether by hammering or rolling, except for the formation of slip-planes. It was otherwise when gold was worked hot, as was to be expected.

The Roman coin of the reign of Constantine, dated about the year A.D. 320, mentioned on p. 334, was probably struck cold. The dies in ancient times were of bronze, and were not suited for striking cold metal, but with the substitution of iron for bronze as the material for dies, about the year A.D. 300, the practice of striking the blanks while they were hot was gradually discontinued.* The "ancient gold coins" referred to in the paper on "The Annealing of Coinage Alloys" as having been struck hot were those of dates before A.D. 300. The evidence from the Constantine coin was therefore in favour of the view that recrystallization of cold-worked metal occurred at atmospheric temperatures with the lapse of time.

The impurities in the specimens examined by Mr. Garland would have greatly retarded recrystallization, and explained the smallness of the amount of recrystallization which had taken place.

Mr. Garland, in reply, thanked Dr. Rose for his remarks, and stated that no doubt the quantity and nature of impurities were determining

* See the writer's article, "Mint," in the *Encyclopædia Britannica*, 11th edition, 1911, vol. xviii. p. 558.

factors in the extent of the recrystallization of metals and alloys at atmospheric, as they were at higher, temperatures.

In that connection it was interesting to observe how, in the dagger described in the second part of the paper, the recrystallization appeared to have confined itself chiefly to the arsenic-rich, oxide-dotted boundaries. A point which appeared to indicate that the cuprous oxide had some influence upon the initiation of recrystallization was that where an oxide globule was found as an inclusion in one of the large copper-rich crystals (called "islands" in the paper) it was observed to be surrounded by a concentric row of small crystals.

In stating that the crystal grains of a cold-worked metal or solid solution were distorted and broken up, he (Mr. Garland) merely sought to describe the more or less extensive elongation of the grains and their division into sections by the intricate systems of cleavages, with, no doubt, the minute intercepting layers of Beilby's amorphous phase. It would seem evident from the crystalline rearrangement and from the minuteness of the new grains observed on etching a cold-worked specimen after slight annealing, that the breaking up of the original grains as described was applicable to gold as well as to other metals, although in some cases recrystallization apparently set in at such low temperatures and so quickly that it prevented observation of the "cataclastic" structure. It was of course often seen in annealed specimens that portions of crystals had been thrust into others by the previous "work."

The author was very glad to have Dr. Rose's authoritative remarks on the Constantine coin.

The writer also expressed his thanks to Mr. F. Johnson for his encouraging communication. He thought that the part of the paper added after the meeting would be of especial interest to Mr. Johnson.

The bismuth in the knife was certainly high, and, strange to say, was not recognizable microscopically. As, however, the alloy was one of six or more components, the author did not attach the same importance to its non-appearance in the microstructure as he would have done had the sample been a purer copper. He intended to have the analysis checked as suggested.

It might be possible that an alloy of the composition stated would stand shaping by a succession of more or less gentle taps, especially if slightly warmed, but not by severe blows or rolling.

INFLUENCE OF PHOSPHORUS ON SOME COPPER-ALUMINIUM ALLOYS.*

By Professor A. A. READ, M.Met., F.I.C.
(University College, Cardiff.)

Valuable information about the properties of the alloys of copper and aluminium has been published by Carpenter and Edwards,† Guillet,‡ and others.

Copper, as is well known, combines with phosphorus to form the compound Cu_3P, and the effect of phosphorus on copper has been investigated, amongst others, by Heyn and Bauer,§ Hiorns, ‖ and Huntington and Desch.¶

With phosphorus, according to Franck,** aluminium forms several phosphides, all of which give off phosphine when treated with water or acids.

Richards †† mentions Shaw's phosphor aluminium bronze with from 0·33 to 5 per cent. of aluminium and 0·05 to 1 per cent. of phosphorus, and he remarks that it has been stated that this alloy has a high conductivity (presumably for electricity), but that he was unable to find any determinations or evidence of any kind to substantiate this statement.

The author thought it would be interesting to investigate the influence of phosphorus on some of the copper-aluminium alloys.

For the purpose of carrying out this research the following materials were procured :—

Electrolytic or cathode copper of very high purity from Messrs. Vivian & Sons, Swansea.

Aluminium from the British Aluminium Co. of guaranteed

* Taken as read at Annual Autumn Meeting, Ghent, August 29, 1913.

† " Eighth Report, Alloys Research Committee," *Proceedings of the Institution of Mechanical Engineers*, 1907.

‡ *Revue de Métallurgie*, 1905, p. 567.

§ *Zeitschrift anorganische Chemie*, 1907, pp. 52, 129.

‖ *Journal of the Society of Chemical Industry*, vol. xxv., 1906, pp. 616 *et seq.*

¶ *Transactions of the Faraday Society*, vol. iv., 1908, pp. 51 *et seq.*

** *Journal of the Chemical Society*, A ii., 1899, p. 102.

†† " Aluminium, Metallurgy and Alloys," 1896, p. 571.

purity, 99·50 per cent., which on analysis gave the following results :—

		Per Cent.
Silicon	. . . .	0·17
Iron .	. . . .	0·18
Sodium	. . . .	0·05

Fifteen per cent. phosphor copper from Messrs. Billington and Newton of Longport.

METHODS OF ANALYSIS.

Estimation of Phosphorus.—Drillings or turnings were dissolved in nitric acid (specific gravity 1·2) and evaporated to dryness.   The mass was dissolved in hydrochloric acid, and the solution was evaporated to a small bulk to remove the greater part of the acid.   After diluting with hot water the copper was precipitated with sulphuretted hydrogen and filtered off, fractional filtration being employed to avoid washing the copper sulphide.   The filtrate was evaporated to a small bulk, the phosphorus precipitated with ammonium molybdate, collected, and weighed.

Estimation of Copper.—The copper was determined both by the iodine-thiosulphate method and by electrolysis, using a rotating cathode.

Estimation of Aluminium.—This has been taken by difference, which probably involves less error than a direct determination.

PRELIMINARY EXPERIMENTS.

Small trial ingots, weighing about 300 grammes, containing varying amounts of copper, phosphorus, and aluminium, were cast in an open chill mould.

The values of the relative hardness, recorded in Table I., were obtained by means of the Shore scleroscope, using the universal hammer.

Rolling Tests.—Pieces having the approximate dimensions 2·5 inches by 0·6 inch by 0·35 inch were cut for rolling. These were rolled cold down to a thickness of 0·1 inch with the necessary annealings, and then rolled down in the cold, if possible, to a strip having a thickness of 0·02 inch.   The

conditions of the tests were made as nearly as possible the same in each case.

TABLE I.—*Composition and Relative Hardness of the Small Ingots.*

No.	Copper per Cent.	Phosphorus per Cent.	Aluminium per Cent.	Relative Hardness.
a	90·36	0·74*	8·90	27
b	88·65	0·18	11·17	28
c	90·84	0·09	9·07	17
d	88·59	0·04	11·37	20
e	95·06	0·50	4·44	13
f	95·35	0·37	4·28	11
g	94·23	0·23	5·54	9
h	95·45	0·09	4·46	7
i	98·53	0·10	1·37	6
j	98·54	0·18	1·28	6
k	98·67	0·40	0·93	6
l	98·68	0·50	0·82	6·5

Judged by their behaviour in the rolling test, the metals in each series stand in the following order :—

Aluminium 1 per cent. :—*j, k, i,* all rolled very well ; *l,* edges slightly serrated.

Aluminium 5 per cent. :—*h* rolled well ; *f* and *g,* edges slighted serrated ; *e,* edges rough and badly cracked.

Aluminium 10 per cent. :—*c* and *d* rolled well to 0·031 inch, and on further rolling broke transversely into small splinters ; *a* and *b* did not roll.

From the information obtained from these preliminary tests, it was decided to investigate on a larger scale the effect of phosphorus on copper containing 5 and 10 per cent. of aluminium respectively.

MELTING AND CASTING OF THE INGOTS.

The copper was melted under charcoal in a Salamander crucible, heated in a coke wind furnace. When all the copper had melted and had attained a good temperature, it was well poled, and the aluminium, which had been heated up almost to its melting point, was forced down into the molten copper. The aluminium at once melted and dissolved in the copper.

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* Distinct smell of phosphine on working.

In each case, on the addition of the aluminium, a marked rise in temperature was observed. The metal was well stirred with a graphite rod, and the required amount of phosphor copper was then added, wrapped up in thin electrolytic sheet copper in the form of a cartridge. The addition of the phosphor copper made the molten metal much more fluid. After again well stirring to ensure the thorough mixing of the phosphor copper the crucible was withdrawn, the metal skimmed, and teemed at as low a temperature as possible, into a circular cast iron chill mould, "following up" with fluid metal from the pot to avoid the pipe which would be caused by shrinkage. The ingots thus cast were $2\frac{1}{4}$ inches in diameter, 18 inches in length, and weighed about 20 lbs. The time from charging the cold copper to teeming never exceeded 50 minutes. The maximum loss of aluminium was 0·2 per cent., and in most cases was less. There was no loss of phosphorus. Eight ingots were cast, and on analysis gave the following results :—

TABLE II.—*Composition of the Ingots.*

No.	Copper per Cent.	Phosphorus per Cent.	Aluminium per Cent.
1	89·94	...	10·06
2	89·90	0·03	10·07
3	89·90	0·05	10·05
4	89·93	0·11	9·96
5	94·98	...	5·02
6	94·97	0·06	4·97
7	94·97	0·09	4·94
8	94·92	0·20	4·88

ROLLING OF THE INGOTS.

Mr. F. Tomlinson of the Broughton Copper Company, Manchester, very kindly undertook to roll the ingots, and I am indebted to him for the following report : " All eight pieces were heated up to the same temperature together, and were rolled down to $\frac{15}{16}$ inch full diameter. Nos. 1 to 6 rolled quite well, but Nos. 7 and 8 broke badly. The cold working, after hot rolling, was carried out on one half piece of each of the hot-rolled rods by drawing through a die (cold drawing). Nos. 1 and 2 appeared to stand the cold working fairly well.

Nos. 3 and 4 broke several times, and also showed a tendency to crack longitudinally. Nos. 5 and 6 were difficult to work cold, but we managed to draw them. Nos. 7 and 8 were of course left out, as they broke down in the hot rolling."

On the return of these bars, it was seen that No. 7 had broken down the worst of all, having cracked badly on being rolled down to $1\frac{1}{4}$ inch diameter. Nevertheless, a piece $2\frac{3}{4}$ inches long, $\frac{1}{2}$ inch wide, and about 0·3 inch thick, which was cut from a sound portion of this bar, was carefully rolled down in the cold with five annealings to 0·012 inch thick without the slightest sign of cracking, and with the edges perfectly smooth. It will also be noticed that under the wire-drawing tests this same metal could be drawn through the last hole, and gave a perfectly sound smooth wire.

WIRE-DRAWING TESTS.

A portion of each rod was turned down to $\frac{3}{16}$ inch diameter for wire drawing, which was carried out first on a small draw-bench, and afterwards by hand.

TABLE III.— *Wire-drawing Results.*

No.	Copper per Cent.	Phosphorus per Cent.	Aluminium per Cent.	Finished at	
				Hole, 1 to 50.	Corresponding Diameter in Inches.
1	89·94	...	10·06	44	0·047
2	89·90	0·03	10·07	43	0·050
3	89·90	0·05	10·05	47	0·042
4	89·93	0·11	9·96	50	0·033
5	94·98	...	5·02	50	0·033
6	94·97	0·06	4·97	50	0·033
7	94·97	0·09	4·94	50	0·033
8	94·92	0·20	4·88	50	0·033

All the wires were quite sound and smooth, and judged by their behaviour in the wire-drawing tests, the alloys of the two series stand in the following order :—

Aluminium 10 per cent.—4, 3, 1, 2. In the case of 2 only a very short length of wire was obtained, even after frequent annealing.

Aluminium 5 per cent.—5, 8, 7, 6. It will be noticed that all the members of this series could be drawn through the last hole (50), diameter 0·033 inch.

TENSILE TESTS.

In the tests about to be described, " H " refers to the cold drawn, " A " to the annealed metal, and " C " to the chill castings. The annealing was carried out by heating the rods, with a pyrometer attached, in a closed gas muffle to 800° C., and keeping them at this temperature for ten minutes. The gas was then turned off, the damper closed, the rods allowed to cool slowly, and were withdrawn when quite cold. No variation in composition was found between the cold-drawn and annealed rods. The chill castings, 1 inch in diameter and 10 inches long, were made in pairs, under the same conditions as the large ingots already described.

The dimensions of the finished test-pieces were as follows :—

Diameter	. 0·564 inch
Gauge length	. 2 inches
Parallel	. 2¼ inches

The tests were carried out on a Buckton universal horizontal testing machine, fitted with a Wicksteed recorder. From the autographic stress-strain diagrams thus obtained the yield points were measured.

The results are given in Tables IV., V., and VI., and are shown graphically in Figs. 1, 2, and 3.

The figures registered for the pure copper-aluminium alloys, which were introduced for the purpose of comparison with similar alloys containing varying amounts of phosphorus, agree very closely with those recorded by Carpenter and Edwards,[*] with the single exception that the yield point obtained by the author for the 5 per cent. aluminium cast bar was somewhat lower.

Aluminium 10 per cent.—Very little, only about 0·2 per cent., phosphorus can be added to this alloy. Above this amount a metal is obtained which on filing or turning gives

[*] " Eighth Report, Alloys Research Committee," *Proceedings of the Institution of Mechanical Engineers*, 1907.

Table IV.—Tensile Tests. Annealed Bars.

Bar No.	Composition			Yield Point, Tons per Square Inch.	Maximum Stress, Tons per Square Inch.	Elongation per Cent. on 2 Inches.	Reduction of Area per Cent.	Remarks.
	Copper per Cent.	Phosphorus per Cent.	Aluminium per Cent.					
1 A	89·94	...	10·06	15·6	30·75	5·1	7·0	Fracture, greyish granular.
2 A	89·90	0·03	10·07	16·5	32·60	6·8	5·5	Fracture, greyish granular. Broke in centre dot.
3 A	89·90	0·05	10·05	16·6	31·24	7·7	7·4	Fracture, greyish granular.
4 A	89·93	0·11	9·96	17·0	30·73	10·0	11·5	Fracture, greyish, finely granular.
5 A	94·98	...	5·02	6·0	24·46	7·1	7·9	Fracture, pale gold, silky. Surface frosted and wavy.
6 A	94·97	0·06	4·97	6·4	24·85	7·9	7·1	Do. do.
8 A	94·92	0·20	4·88	6·8	25·57	8·2	7·7	Do. do.

TABLE V.—*Tensile Tests. Cold Rolled Bars.*

Bar No.	Composition.			Yield Point, Tons per Square Inch.	Maximum Stress, Tons per Square Inch.	Elongation per Cent. on 2 Inches.	Reduction of Area per Cent.	Remarks.
	Copper per Cent.	Phosphorus per Cent.	Aluminium per Cent.					
1 II	89·94	...	10·06	42·0	44·28	9·0	12·4	Fracture, greyish granular. Surface slightly wavy.
2 II	89·90	0·03	10·07	44·4	45·64	6·7	8·4	Fracture, greyish granular. Surface smooth.
3 II	89·90	0·05	10·45	...	37·74	0·6	2·1	Fracture, greyish granular. Surface smooth.
4 II	89·93	0·11	9·96	44·7	45·60	6·9	4·6	Fracture, greyish granular. Surface smooth. (This bar has evidently been overdrawn.)
5 II	94·98	...	5·02	17·4	27·20	64·0	75·1	Fracture, pale gold, silky, cup and cone. Surface frosted.
6 II	94·97	0·06	4·97	21·0	31·26	45·4	70·4	Do. do.

Table VI.—Tensile Tests. Chill Castings.

Bar No.	Composition.			Yield Point, Tons per Square Inch.	Maximum Stress, Tons per Square Inch.	Elongation per Cent. on 2 Inches.	Reduction of Area per Cent.	Remarks.
	Copper per Cent.	Phosphorus per Cent.	Aluminium per Cent.					
9 C	89·55	0·18	10·27	5·6	27·12	8·3	13·1	Fracture, greyish brown, radially crystalline. Surface slightly wavy.
12 C*	89·65	0·40	9·95	8·0	25·92	11·1	17·0	Do. do. do.
10 C*	89·80	0·50	9·70	5·8	18·72	3·9	9·2	Fracture, greyish brown, radially crystalline. Surface smooth.
16 C	91·88	...	5·12	5·0	18·73	68·0	58·2	Fracture, pale gold, silky. Surface very wavy.
17 C	94·79	0·25	4·96	5·4	18·08	35·2	31·5	Fracture, pale gold, silky, radially crystalline. Surface wavy.
11 C	94·34	0·52	5·14	6·3	21·41	35·2	37·8	Fracture, grey, radially crystalline. Surface wavy.
13 C	93·95	0·75	5·30	6·8	20·00	19·6	20·8	Fracture, grey granular. Surface wavy.
14 C	93·70	1·02	5·28	9·2	15·68	9·7	13·0	Fracture, grey, granular. Surface slightly wavy.

* Distinct smell of phosphine on turning down these test-pieces.

off an unmistakable odour of phosphine, due to the decom-
position of aluminium phosphide.
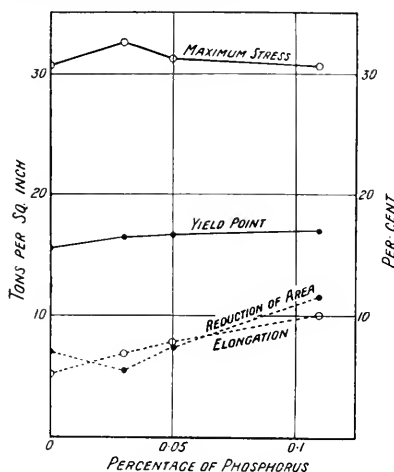
FIG. 1.—Tensile Tests.
Aluminium 10 per cent. Rolled and annealed.

Annealed.—The effect of very small quantities of phosphorus
is to raise the yield point a little, and to increase the elonga-
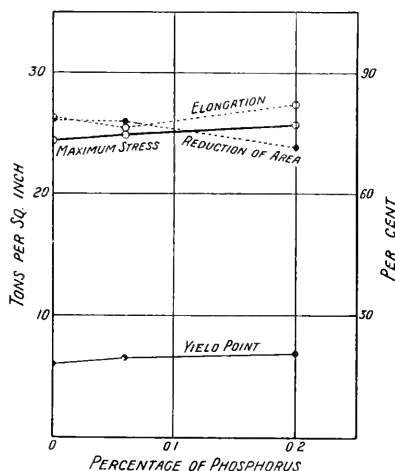
FIG. 2.—Tensile Tests.
Aluminium 5 per cent. Rolled and annealed.

tion and reduction of area considerably, while the maximum
stress remains practically the same.

Z

Cold Drawn Rods.—The yield point and maximum stress are unaltered, but the elongation and reduction of area are lowered considerably by increasing amounts of phosphorus.

Aluminium 5 per cent.—A much larger amount of phosphorus can be added to a 5 per cent. aluminium alloy than to a 10 per cent. one. The cast bars containing 1 per cent. of phosphorus were worked without the slightest trace of phosphine being detected.
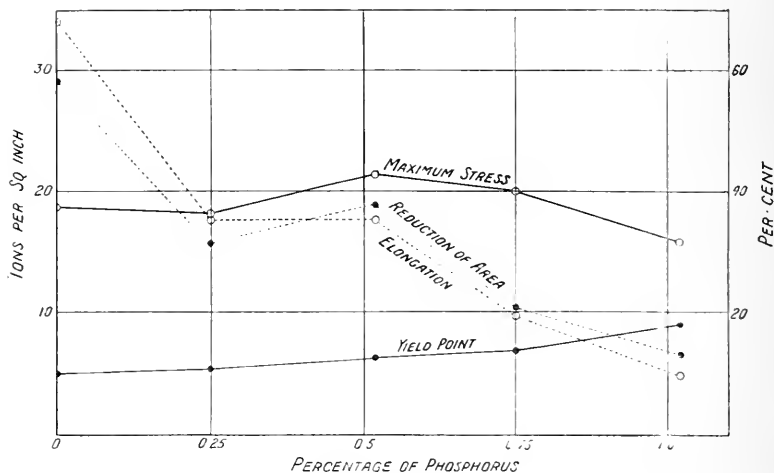
FIG. 3.—Tensile Tests.
Aluminium 5 per cent. Cast.

Annealed.—The yield point and maximum stress rise a little, and the reduction of area is lowered, as the phosphorus increases. As regards elongation, No. 8A, containing 0·20 per cent. of phosphorus, registered a slightly higher result than the corresponding alloy without phosphorus.

Chill Castings.—With increasing amounts of phosphorus the yield point rises continuously, the ultimate stress attains a maximum at 0·52 per cent. of phosphorus, but the elongation and reduction of area fall rapidly. Fig. 4 shows the appearance of some of the specimens broken in tensile tests.

Aluminium 5 per cent.

16c	17c	14c	5a	8a
Nil	0·25	1·02	nil	0·20

Phosphorus per cent.

Fig. 4.

Alternating Stress Tests.

The author is indebted to Professor Arnold for these results. The dynamic tests obtained under standard conditions on the Arnold machine are given in Table VII.

The detrimental effect produced by annealing the 10 per cent. aluminium alloys is well exemplified by the poor dynamic properties shown by the members of this series under the alternating stress test.

TABLE VII.—*Alternating Stress Tests.*

No.	Composition.			Alternations endured under Standard Conditions.					
	Copper per Cent.	Phosphorus per Cent.	Aluminium per Cent.	Annealed.			Cold Rolled.		
				First Test.	Second Test.	Mean.	First Test.	Second Test.	Mean.
1	89·94	...	10·06	38	38	38	184	278	231
2	89·90	0·03	10·07	36	36	36	214	440	327
3	89·90	0·05	10·05	42	44	43	500	376	438
4	89·93	0·11	9·96	38	48	43	...	...	...
5	94·98	...	5·02	720	762	741	800	746	773
6	94·97	0·06	4·97	774	698	736	714	622	668
7	94·97	0·09	4·94	1000	762	881	...	...	...
8	94·92	0·20	4·88	868	858	863	...	...	...

HARDNESS TESTS.

These numbers have been determined as far as possible both by the Shore scleroscope, using the universal hammer, and Brinell methods. The specimens tested were cylinders, about 2 inches high and 1 inch in diameter, with polished surfaces. For the determination of hardness by the Brinell method, the author is indebted to Mr. H. I. Coe, M.Sc., of the Birmingham University. These tests were carried out according to the standard conditions, using a 10 millimetre ball under a load of 3000 kilogrammes, and the hardness numbers have been calculated as follows:—

$$\frac{\text{Load (in kilogrammes)}}{\text{spherical area of the concavity (in square millimetres)}}.$$

The hardness numbers obtained by both the scleroscope and Brinell methods are given in Table VIII. These results are shown graphically in Fig. 5, where the Brinell numbers are represented by dots and a continuous line, and the scleroscope readings by small circles and a dotted line. The relative hardness numbers recorded by both methods are in fairly close agreement, the lines through the two sets of readings running nearly parallel to each other. The scleroscope numbers for

TABLE VIII.—*Hardness Tests.*

| Bar No. | Composition. | | | Hardness Numbers. | | | | | |
| | Copper per Cent. | Phosphorus per Cent. | Aluminium per Cent. | Scleroscope. | | | Brinell. | | |
				Annealed.	Cold Drawn.	Chill Castings.	Annealed.	Cold Drawn.	Chill Castings.
1	89·94	...	10·06	21·5	33·0	20·0	127	186	...
2	89·90	0·03	10·07	23·0	35·0	19·5	158	196	...
3	89·90	0·05	10·05	21·0	37·5	19·5	140	209	...
4	89·93	0·11	9·96	20·0	36·0	19·5	128	205	...
9	89·55	0·18	10·27	...	...	24·5	...	...	156
12	89·65	0·40	9·95	...	...	20·0	...	...	130
10	89·80	0·50	9·70	...	...	22·5	...	...	133
5	94·98	...	5·02	9·0	17·0	9·0	77	114	...
6	94·97	0·06	4·97	9·0	27·0	8·5	75	149	...
7	94·97	0·09	4·94	9·0	...	8·5	76	...	...
8	94·92	0·20	4·88	9·2	...	8·5	79	...	...
16	94·88	...	5·12	...	...	8·5	...	...	...
17	94·79	0·25	4·96	...	...	9·0	...	...	74
11	94·34	0·52	5·14	...	...	10·0	...	...	79
13	93·95	0·75	5·30	...	...	12·5	...	...	89
14	93·70	1·02	5·28	...	...	13·7	...	...	94
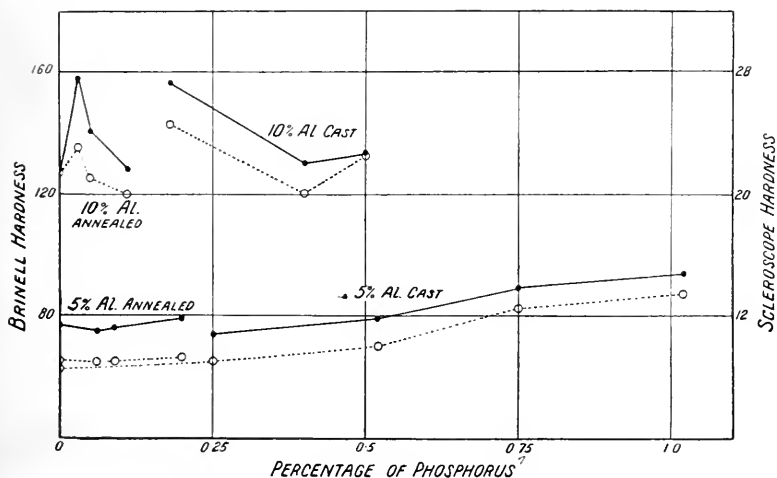
FIG. 5.—Hardness. Brinell and Scleroscope Tests.

the cold-drawn material are, as usual, proportionally higher than those obtained by the Brinell method.

Aluminium 10 per cent. — With the small increasing amounts of phosphorus, the hardness of the annealed bars is unaltered, but with the cold-drawn bars the hardness is raised slightly.

Aluminium 5 per cent. — Small quantities of phosphorus do not alter the hardness of the four annealed bars of this series. In the case of the chill castings the hardness does not change until after 0·25 per cent. of phosphorus is passed, and then it is raised considerably by increasing amounts of phosphorus.

CONDUCTIVITY FOR ELECTRICITY.

The resistance of definite lengths of the wires, made as described under " wire drawing " and subsequently annealed, was measured by the Wheatstone bridge method with the aid of a carefully standardized resistance box.   The diameters of the wires were afterwards obtained by weighing a measured length in air and water.   The composition of the wires on analysis was found to be identical with that of the rods from which they were drawn.   The results are given in Table IX., which shows the specific resistances of the alloys in microhms (ohms $\times 10^{-6}$), and also the percentage conductivity of each member of the series relative to that of pure copper at the same temperature.

TABLE IX.—*Electrical Conductivities at* $11\cdot5°$ *C.*

No.	Composition.			Specific Resistance (Ohms $\times 10^{-6}$).	Conductivity (Copper = 100).
	Copper per Cent.	Phosphorus per Cent.	Aluminium per Cent.		
1	89·94	...	10·06	10·27	15·9
3	89·90	0·05	10·05	10·53	15·6
4	89·93	0·11	9·96	10·75	15·2
5	94·98	...	5·02	9·85	16·6
6	94·97	0·06	4·97	10·36	15·8
7	94·97	0·09	4·94	11·02	14·9
8	94·92	0·20	4·88	11·67	14·0

It will be noticed that the conductivity of the 5 per cent. alloy is only very slightly greater than that of the alloy containing 10 per cent. of aluminium. The effect of phosphorus in both cases is to diminish the conductivity. In the case of the 5 per cent. alloy the diminution is far more marked, being, for a given amount of phosphorus, more than twice as great as in the 10 per cent. alloy.

MELTING POINTS.

The melting points were determined with a thermo-electric couple and a direct-reading millivoltmeter. The results, which are tabulated in Table X., show that as the phosphorus increases, in each series of the alloys, the melting points fall.

TABLE X.—*Melting Points.*

No.	Copper per Cent.	Phosphorus per Cent.	Aluminium per Cent.	Melting Point, Degrees C.
1	89·94	...	10·06	1038
4	89·93	0·11	9·96	1030
9	89·55	0·18	10·27	1025
10	89·80	0·50	9·70	1019
5	94·98	...	5·02	1054
15	94·55	0·25	5·20	1045
11	94·34	0·52	5·14	1042
14	93·70	1·02	5·28	1030

CORROSION TESTS.

Cold-rolled and annealed plates of metal, $1·8 \times 0·6 \times 0·1$ inch, equal to about 3 square inches of surface, were used for these tests. Each of these plates, after being polished and thoroughly cleaned, was weighed and suspended from a glass hook attached to a piece of wood, which rested on the top edges of a porcelain tank. Fig. 6 shows this arrangement, which was used for both the fresh- and sea-water experiments. At the end of the tests the plates were carefully cleaned, dried, and weighed.

Fresh-water Tests.—A gentle stream of tap-water was kept flowing continuously through the tank for 112 days, during which time the plates were now and again taken out and gently rubbed.
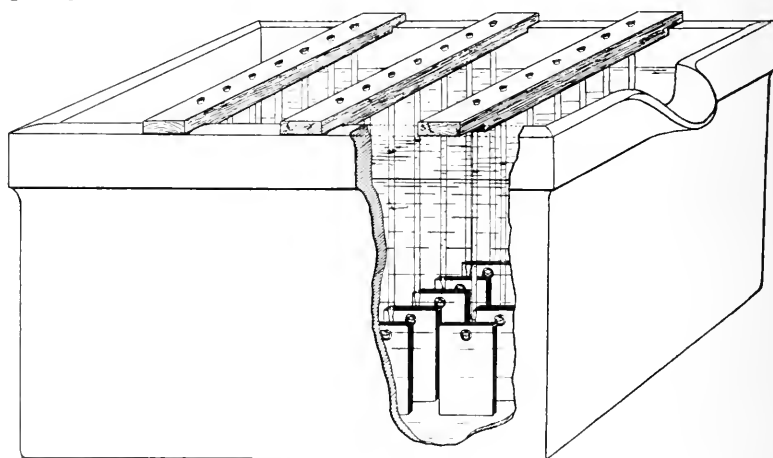
FIG. 6.

The chemical composition, as given below, shows the tap-water to be " soft " and of high quality.

Constituent.							Grains per Gallon.
Free ammonia	.	.	.	.	.	.	0·0007
Albuminoid ammonia	.	.	.	.	.	.	0·0035
Silica	.	.	.	.	.	.	0·035
Ferric oxide	.	.	.	.	.	.	0·07
Sodium chloride	.	.	.	.	.	.	0·68
Magnesium chloride	.	.	.	.	.	.	0·25
Magnesium carbonate	.	.	.	.	.	.	0·36
Calcium sulphate	.	.	.	.	.	.	0·58
Calcium carbonate	.	.	.	.	.	.	2·15

The results are given in Table XI., where it will be seen that this very pure tap-water had an exceedingly small action on the alloys. The plates were slightly tarnished, but were still smooth and showed no signs of corrosion.

Sea-water Tests.—The sea water, which was obtained from a bay in the Bristol Channel, was changed every fortnight, and at the same time the plates were taken out and gently rubbed. The duration of the trials was ninety-eight days.

TABLE XI.—*Corrosion Tests.*

| No. | Composition | | | Loss in Weight in lbs. per Square Foot per Month. | | | |
| | Copper per Cent. | Phosphorus per Cent. | Aluminium per Cent. | Sea Water. | | Fresh Water. | |
				Annealed.	Cold Rolled.	Annealed.	Cold Rolled.
1	89·94	…	10·06	0·00103	0·00020		
d	88·59	0·04	11·37	0·00026	0·00025		
c	90·84	0·09	9·07	0·00025	0·00023		
δ	94·98	…	5·02	0·00042	0·00039	under 0·00005	under 0·00005
h	95·45	0·09	4·46	0·00031	0·00034		
g	94·23	0·23	5·54	0·00026	0·00029		
f	95·35	0·37	4·28	0·00029	0·00031		
j	98·54	0·18	1·28	0·00050	0·00054		
k	98·67	0·40	0·93	0·00055	…		

The results are recorded in Table XI., and it will be noticed that the effect of small quantities of phosphorus is to reduce the loss of weight due to corrosion of the alloys by the sea water. The plates after their immersion in the sea water were all smooth but darker in colour ; the 10 per cent. aluminium alloys assumed a bronze colour tint, those with 5 per cent. of aluminium a dull red colour, while the 1 per cent. aluminium alloys were coated with a fine dark red deposit, which could be easily removed on rubbing.

Microscopical Features of the Alloys.

The constitution of the two alloys with 5 and 10 per cent. of aluminium is now well known to be as follows :—

The 5 per cent. alloy contains only the α constituent, which is a solid solution of aluminium in copper, and the 10 per cent. alloy consists of the α and β constituents.

The accompanying photomicrographs were all taken by direct light, and show the structure of some of the alloys. The specimens were etched with an acid solution of ferric chloride.

Aluminium 10 per Cent.

Micrographs Nos. 1. 2, and 3 respectively represent the metal containing 0·11 per cent. of phosphorus as " cast," " cold drawn," " rolled and annealed." No phosphide could be detected, hence all the phosphorus is in solution. The structures with the α constituent, gold colour, and the β dark, are identical in appearance with a 10 per cent. aluminium alloy without phosphorus. In the alloy with 0·18 per cent. of phosphorus no phosphide could be detected, but with 0·4 and 0·5 per cent. of phosphorus (the two metals which gave off phosphine on working) light spots of phosphide, which must contain aluminium phosphide, could be seen in the β constituent.

Aluminium 5 per Cent.

Micrograph No. 4 shows the structure of copper with 5 per cent. of aluminium as cast, and consists solely of the pale gold crystals of the α constituent.
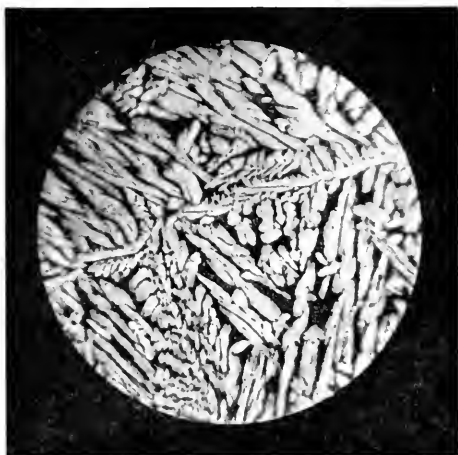
MICROGRAPH No. 1.

Copper, 89·93 per cent. ; Phosphorus, 0·11 per cent. ;
Aluminium, 9·96 per cent.
Cast.
Magnified 100 diameters.

MICROGRAPH No. 2.

Copper, 89·93 per cent. ; Phosphorus, 0·11 per cent. ;
Aluminium, 9·96 per cent.
Cold rolled.
Magnified 100 diameters.
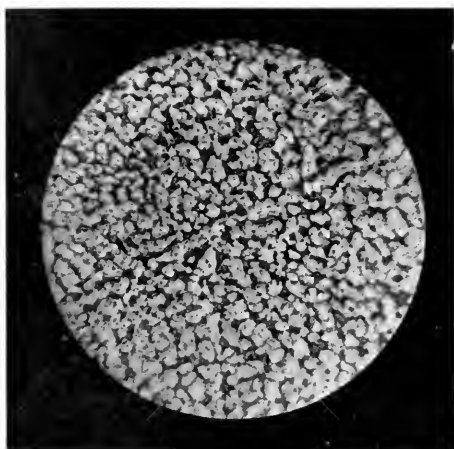
MICROGRAPH No. 3.

Copper, 89·93 per cent. ; Phosphorus, 0·11 per cent. ;
Aluminium, 9·96 per cent.
Rolled and annealed.
Magnified 100 diameters.

MICROGRAPH No. 4.

Copper, 94·88 per cent. ; Aluminium, 5·12 per cent.
Cast.
Magnified 60 diameters.

Micrograph No. 5. This alloy contains 0·2 per cent. of phosphorus. The cast metal shows the phosphide separated out along the boundaries of the crystals. The phosphorus has the further effect of causing the *a* solution to assume a bronze colour on etching, and consequently this constituent appears dark in the photographs.

Micrograph No. 6 is a 5 per cent. aluminium alloy without phosphorus, which has been annealed. This structure is
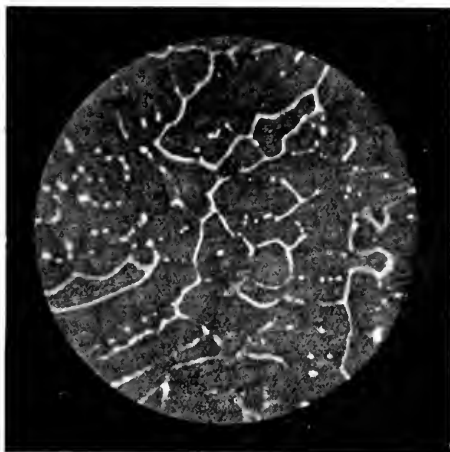
MICROGRAPH No. 5.

Copper, 94·92 per cent. ; Phosphorus, 0·20 per cent. ;
Aluminium, 4·88 per cent.
Cast.
Magnified 100 diameters.

typical of the annealed alloys containing up to 0·20 per cent. of phosphorus, the phosphide being in solution. With 0·25 per cent. of phosphorus the phosphide is not all dissolved, and a few spots can still be detected after annealing.

Micrograph No. 7 exhibits the structure of a cold-drawn rod containing 0·06 per cent. of phosphorus.

Micrographs Nos. 8, 9, and 10 all contain 0·52 per cent. of phosphorus. No. 8 is the cast metal with the phosphide separated out along the boundaries of the crystals. The effect of annealing for twenty minutes at 800° C. is shown in No. 9, where it will

MICROGRAPH No. 6.

Copper, 94·98 per cent. ; Aluminium, 5·02 per cent.
Rolled and annealed.
Magnified 100 diameters.
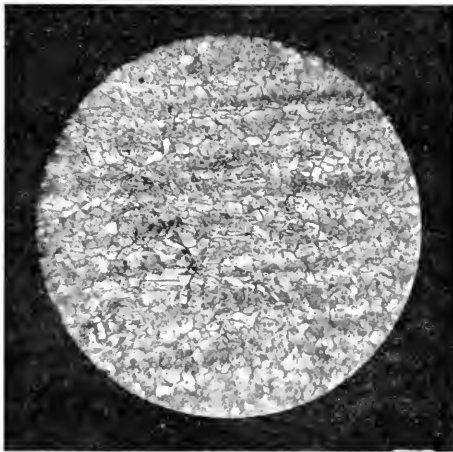
MICROGRAPH No. 7.

Copper, 94·97 per cent. ; Phosphorus, 0·06 per cent. ;
Aluminium, 4·97 per cent.
Cold rolled.
Magnified 100 diameters.

be seen that the phosphide has begun to ball up. On further annealing for another twenty minutes at the same temperature, the phosphide has completely balled up, still leaving the boundaries of the crystals well defined.

In connection with this part of the subject, attention may be drawn to a comparison of the solubility of phosphorus in copper, and in copper containing aluminium. The limit of the solubility of phosphorus in copper, according to Huntington

MICROGRAPH No. 8.
Copper, 94·34 per cent.; Phosphorus, 0·52 per cent.;
Aluminium, 5·14 per cent.
Cast.
Magnified 100 diameters.

and Desch,* is 0·175 per cent., whereas in the 5 per cent. aluminium alloy with 0·2 per cent. of phosphorus the phosphide is all in solution, and it is only when 0·25 per cent. of phosphorus is reached that a few spots of phosphide can be detected, the greater part being in solution.

In conclusion, the author has to tender his sincere thanks to Mr. R. H. Greaves, M.Sc., for his valuable help and assistance with the work of this research.

* *Transactions of the Faraday Society*, 1908, vol. iv. p. 56.
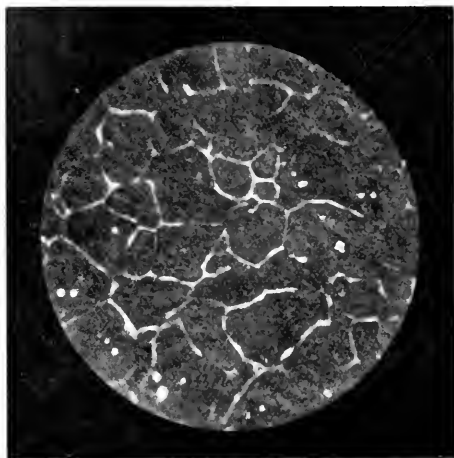
MICROGRAPH No. 9.
Copper, 94·34 per cent. ; Phosphorus, 0·52 per cent. ;
Aluminium, 5·14 per cent.
Annealed for 20 minutes at 800° C.
Magnified 100 diameters.
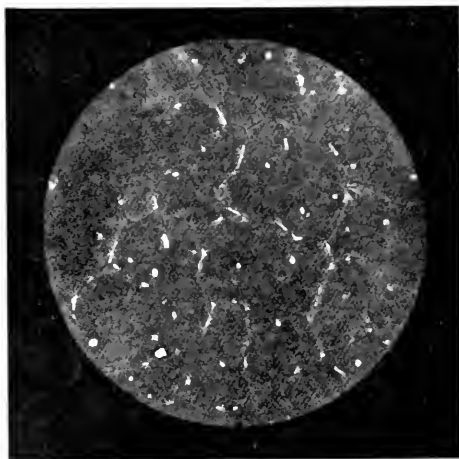
MICROGRAPH No. 10.
Copper, 94·34 per cent. ; Phosphorus, 0·52 per cent.
Aluminium, 5·14 per cent.
Annealed for 40 minutes at 800° C.
Magnified at 100 diameters.

COMMUNICATION.

Mr. F. Johnson, M.Sc. (Birmingham), wrote that he had been greatly interested in Professor Read's paper, upon which a verbal discussion would have been very welcome.

The alternating stress tests given in Table VII. were extremely interesting. It was such a rare event in metallurgical work to find that cold-rolled material gave greater toughness than the annealed material. Professor Read laid very little stress on that remarkable exception to the general rule, and so far as he (Mr. Johnson) had been able to see, had offered no explanation. He would be very glad if the author could throw some light on that extraordinary feature of the work.

The increase of resistance to alternating stresses conferred by phosphorus on the 10 per cent. aluminium alloys was very noteworthy, especially as the phosphorus had been added after, and not before, the aluminium. He (Mr. Johnson) would have suggested the addition of phosphorus before the aluminium, in order to free the copper from oxide, and so prevent the formation of alumina, which was regarded as so detrimental. It was difficult to understand how the improvement was brought about by phosphorus, since it could not have been a matter of deoxidation, all deoxidation having been effected by the aluminium. It would be very interesting to know whether, in promoting fluidity—as phosphorus undoubtedly did—a disengagement of the mechanically enclosed alumina was effected. Some of the phosphorus would undoubtedly become oxidized, and, entering into the composition of the aluminous dross, would still further facilitate its separation by producing a slag of lower melting point and greater fluidity.

The heterogeneity of the cold-rolled material, as revealed in the alternating stress tests, was very marked, and the writer would be very pleased if Professor Read would explain that.

On p. 367 the author referred to the limit of solubility of phosphorus in copper, and quoted Huntington and Desch as placing that limit at 0·175 per cent.

He would refer the author to the paper by Hudson and Law, "A Contribution to the Study of Phosphor Bronze," * in which the authors stated that a phosphor-copper containing 0·9 per cent. phosphorus had an almost homogeneous structure after annealing.

The writer regretted that the alloys with 1 per cent. aluminium and phosphorus had not been included in the larger scale investigation, particularly as the results of that investigation on the alloys with higher percentages of aluminium would not bear any recommendation to manufacturers of such alloys as regarded the serviceableness of adding phosphorus.

Professor Read, replying to Mr. Johnson's communication, wrote that he could not regard as unexpected the fact that the behaviour of the

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* *Journal of the Institute of Metals*, No. 1, 1910, vol. iii. p. 61.

cold rolled material containing 10 per cent. of aluminium in the alternating tests was better than that of the annealed. It was a well-known fact, emphasized by Carpenter and Edwards,* that annealing ruined the 10 per cent. aluminium alloys. Reference to the figures in Tables IV. and V. would show that the yield point, maximum stress, elongation, and reduction of area were each greater in the cold rolled state, so that increased resistance to alternating stress was only to be expected. As regards Mr. Johnson's remarks on the effect of the addition of phosphorus, he was of opinion that the first action of the phosphorus was to promote fluidity, but as stated in the early part of the paper, no appreciable amount of phosphorus was lost by oxidation.

* "Eighth Report, Alloys Research Committee." *Proceedings of the Institute of Mechanical Engineers*, 1907, pp. 70, 177, 178.

THE DETERMINATION OF OXYGEN IN COPPER AND BRASS.*

By T. WEST, M.Sc. (THE UNIVERSITY, MANCHESTER).

DURING the last few years several papers dealing with the presence of oxygen in copper and its alloys have been read before the Institute of Metals, and both in the papers and in the ensuing discussions a further recognition of the influence of oxygen on the properties and behaviour, not only of copper, but of metals and alloys in general, has been urged upon all who are interested in their manufacture and use.

Oxygen may by its presence in a metal exert a beneficial influence, as in the case of copper containing arsenic, where it has been found that the presence of a certain amount of oxygen in proportions determined by the quantity of arsenic is most beneficial. Rose also states that a small quantity of oxygen in the form of oxide of lead is most useful in preventing the brittleness of standard gold. But more generally the oxygen is present owing to unavoidable oxidizing effects produced during the various manipulations involved in manufacture. In the latter case, although the amount may be very small, yet it may have most damaging effects on the " life " of the casting in which it is embedded.

As it is known that the presence of oxygen has certain effects on alloys, further assistance in the explanation of its influence is given by a knowledge of the manner in which the oxygen occurs in the mass of metal. A microscopic examination of the substance often explains the apparently unaccountable behaviour of some casting. With the alloys of copper such an examination shows that the oxygen enters intimately into the structure of the alloy, and though interpretations of the manner in which it exists chemically may vary, it undoubtedly prevents other impurities exerting such a harmful influence on the mechanical and physical properties of the copper. In other cases, where the presence of the oxide is

* Taken as read at Annual Autumn Meeting, Ghent, August 29, 1913.

accidental, it is generally observed scattered amongst the crystals, but more often along the crystal boundaries, thus acting as a source of weakness, while, as so lucidly explained by Law, ([1]) quantities of oxide, often unobserved in microscopic examination owing to their minute amounts or to removal during preparation for examination, may be responsible for many cases of corrosion.

For a thorough investigation of the influence of oxygen, the determination of its absolute amount is necessary before strictly comparable tests can be carried out. With this object in view some experiments have been carried out, the work in connection with which is embodied in this paper.

The determination of oxygen in copper now presents little difficulty, as a satisfactory method is known which gives results of the required degree of accuracy. Greaves, ([2]) in an appendix to a paper on "The Influence of Oxygen in Copper containing Arsenic and Antimony," gives an excellent summary of the methods for determining oxygen in copper, which renders it unnecessary for full details to be given here. In this summary he classifies the methods for the determination of the oxygen into two classes according as the object is :—

(*a*) To estimate the oxygen existing as cuprous oxide, or

(*b*) The estimation of the total oxygen.

With regard to the methods for determining the cuprous oxide he says: "In all the above methods there is the uncertainty as to whether the cuprous oxide actually found exists in the copper wholly as free oxide or partly combined with oxides of arsenic or antimony." It is this uncertainty which renders these methods to a large extent useless, because a corresponding uncertainty exists from microscopic examination as to the chemical condition in which the oxygen exists, and so the methods which give the total oxygen find more favour, for the manufacturer desires to know the amount of oxygen, irrespective of its mode of existence, which will neutralize the ill effects of other impurities and have the least tendency to be harmful itself.

The usual method for the determination of the total oxygen is to reduce the heated metal by a stream of hydrogen.

Various workers have modified the method which was introduced by Hampe, (³) who with elaborate precautions heated small pieces of copper in a current of hydrogen and ascertained the loss in weight of the copper. Archbutt (⁴) established the accuracy of the method, demonstrating that equally accurate results were obtained by noting the loss in weight of the copper or weighing the water formed. He also showed that the reduction is more rapidly accomplished the finer the state of division of the copper, which need not be heated above redness. Blount (⁵) melted the copper in a current of hydrogen, while Dickson (⁶) melted the copper with purified tin in a current of the gas, both experimentalists weighing the water formed.

Turner (⁷) attempted to apply the method of reduction by hydrogen to the estimation of oxygen in brass, but showed that certain difficulties arise which are absent in the case of copper and so render the method useless. At the outset he showed that any oxygen in brass very probably exists in the form of scattered particles of zinc oxide, which microscopic examination fails to detect owing to their being rubbed out during the operation of polishing. On this assumption he showed that it was useless to attempt to determine the oxygen by ignition in a current of hydrogen. The small amount of zinc oxide likely to exist is reduced by the hydrogen, but on reaching the cooled part of the tube the reverse reaction occurs, which results in the zinc oxide being deposited as a fine film on the glass tube, and consequently with no increase in weight of the absorption bulbs. In conclusion Turner says : " It is, therefore, evident that no accurate determination of oxygen in brass can be made by adopting the methods which are suitable for copper," and " A description of a simple and direct process for the accurate determination of oxygen in brass would be appreciated by many who are interested in the subject."

At the suggestion of Professor Carpenter the author carried out some further experiments to obtain, if possible, more conclusive results as to the amount of oxygen to be found in ordinary brass. In place of hydrogen as the reducing agent carbon monoxide was decided upon, and to test the accuracy

of this method some specimens of oxidized copper were reduced
by hydrogen and the results thus obtained compared with
those obtained when the reduction was accomplished by carbon
monoxide.   Afterwards tests were carried out with brass sub-
stituted for copper.

DETERMINATION OF OXYGEN IN COPPER, USING HYDROGEN AS REDUCING AGENT.

For experimental purposes alloys of copper and oxygen
were made by dissolving varying quantities of pure cupric
oxide in the same weight of pure electrolytic copper.   From
these mixtures, turnings, obtained by using a lathe working at
a low gear to prevent oxidation, were taken for the estimation
of oxygen.

Fig. 1 shows the apparatus used in the determination of the
oxygen.   Hydrogen, generated from pure zinc and dilute sul-
phuric acid, was purified by passing through a train of wash
bottles containing solutions of lead acetate, silver nitrate, and
caustic potash, and through a further tube containing pieces
of solid potash.   Traces of oxygen were removed by passing
through a heated Jena glass tube containing copper gauze and
absorbing the water formed in sulphuric acid, while the gas
finally passed through a tube of calcium chloride.   The flow of
the gas was regulated by a tap at A.   All the parts of the
apparatus were sealed together or connected by means of
ground glass joints secured by rubber bands.   The combustion
tube, made of silica, was heated in a gas furnace, and the
water formed absorbed in a stoppered U-tube containing
calcium chloride.   A similar U-tube was attached to act as
guard tube, and an aspirator was attached to the guard tube.
The procedure was to weigh about 10 grammes of the copper
drillings into a boat, introduce into the combustion tube, and
attach the absorption tube, guard tube, and aspirator.   A
slow current of hydrogen was passed for half an hour, the
U-tube detached and weighed.   On re-attachment the current
was passed for about a quarter of an hour, and the reduction
then commenced by heating the silica tube to about 750°
(measured by a thermocouple).   After heating for an hour

FIG. 1.

CALCIUM CHLORIDE TUBES.

COMBUSTION TUBE

KOH

COPPER

KOH

$H_2 SO_4$

CAUSTIC POTASH

SILVER NITRATE

LEAD ACETATE

HYDROGEN GENERATOR

TO ASPIRATOR

FIG. 2.

$H_2 SO_4$

KOH

COMBUSTION TUBE

$H_2 SO_4$

Cu GAUZE KOH

$H_2 SO_4$

KOH

KOH COPPER GAUZE

KOH

CO
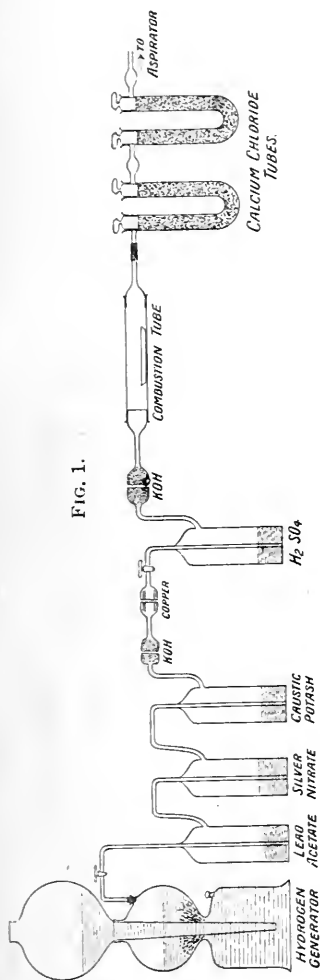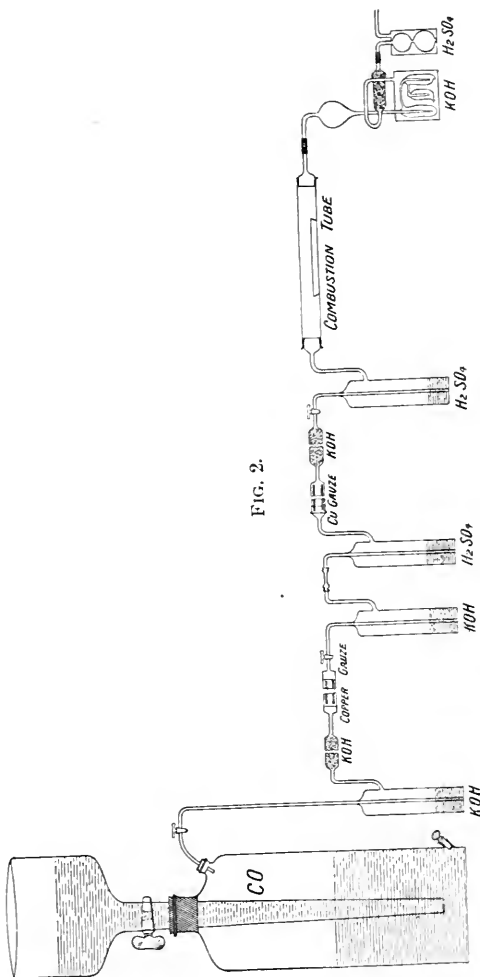
the combustion was stopped, but the current was passed for a further quarter of an hour. The absorption tube was then detached, carefully wiped, and weighed. From time to time a blank experiment was carried out by heating a roll of previously deoxidized copper gauze and employing the same precautions as above. In these experiments an hour's ignition resulted in the weight of the U-tube remaining absolutely constant.

The results of the determinations carried out in duplicate with these specimens are given :—

				Oxygen.		
				A.	B.	C.
				Per Cent.	Per Cent.	Per Cent.
1st Result	.	.	.	0·083	0·175	0·260
2nd Result	.	.	.	0·083	0·176	0·258

Determination of Oxygen in Copper, using Carbon Monoxide as Reducing Agent.

Murmann first used this gas for reducing oxidized copper. He heated copper in a current of carbon monoxide, and concluded that to completely reduce the metal it must be afterwards heated in a current of hydrogen. He calculated the oxygen by weighing the copper before and after reduction.

Lucas also determined the oxygen in copper by fusing a piece of copper, along with pure tin, in an electric furnace in a current of CO, and weighing the carbon dioxide formed. He stated that results agreeing with those determined by ignition in hydrogen were obtained.

A similar method to that of Lucas has been used in the present series of experiments. Pure carbon monoxide was prepared by heating a mixture of sodium formate and sulphuric acid and collecting the gas in an air-tight gasometer, whence the gas was passed through a series of purifying and drying tubes, as shown in Fig. 2. The carbon monoxide was passed successively through the following reagents : a solution

of caustic potash and solid pieces of caustic potash to absorb carbon dioxide, a heated Jena glass tube containing copper gauze to remove oxygen by causing it to form carbon dioxide, a solution of caustic potash to absorb any carbon dioxide formed in the previous tube, strong sulphuric acid to dry the gas, another heated Jena glass tube to remove the last trace of oxygen, a tube containing solid potash, and a drying bottle of sulphuric acid. On leaving the last bottle the stream of gas was regulated by a tap, after which it passed through the actual combustion tube, and then along with any carbon dioxide formed through the absorption apparatus. The latter consists of bulbs containing dilute caustic potash combined with a tube filled with fine pieces of calcium chloride. A guard tube containing strong sulphuric acid was attached to the apparatus. As with the hydrogen apparatus, no rubber connections were used except where the absorption bulb was attached, and the various parts were either sealed together or joined by ground glass joints. The combustion tube was of glazed silica, and rested in the porcelain tube of an electric furnace fitted with water-cooled ends. The furnace temperature, which could be varied by a rheostat, was measured by a thermocouple, the wires of which passed between the porcelain and silica tubes and were connected to a pyrometer.

In all the experiments where carbon monoxide was the reducing agent, great importance was attached to the blank experiments which were carried out at frequent intervals. In such an experiment about 10 grammes of previously deoxidized copper were placed in the combustion tube, and when the absorption bulbs remained constant in weight while the gas passed at a fairly rapid rate (2 bubbles per second) for at least an hour the furnace was at once heated. The temperature was raised at 1050° and held there for at least two hours, after which the absorption bulbs showed an increase in weight never exceeding 0·0002 gramme.

From 5 to 10 grammes of the copper drillings were inserted in the silica tube, the absorption bulbs and guard tube attached, and the apparatus tested to see that it was quite airtight. A steady current of gas was passed before heating the specimen, and when this current passing for an hour caused

no increase in weight of the absorption bulbs the combustion was started. The furnace was then heated to a temperature of 900° and held there for about two hours, while the gas was allowed to pass another half-hour after ceasing to heat the furnace. The absorption apparatus was carefully disconnected and weighed full of carbon monoxide. To ensure complete reduction, the combustion may be carried on for a further hour.

In several experiments the conditions were varied somewhat. In some cases the temperature of combustion was raised to 1050° and in others the copper was mixed with about one-fifth its weight of tin previously purified by melting in a stream of carbon monoxide; by heating to 900° the two metals mix to form an alloy which is molten at this temperature. Concordant results were obtained under the various conditions. The following results may be compared with those on p. 376 :—

	A.	B.	C.
	Per Cent.	Per Cent.	Per Cent.
Heating to 900° . . .	0·079	0·172	......
Heating to 1050° . . .	0·081	0·173	......
Heating with tin to 900° . .	0·081	0·173	0·260

ACTION OF CARBON MONOXIDE ON BRASS.

As there is every likelihood of any oxygen in brass existing as zinc oxide, the behaviour of zinc oxide may be considered. Moissan has shown that zinc oxide is volatile in the electric furnace, but in an atmosphere of carbon monoxide and under the experimental conditions this effect was found to be negligible. A more important factor is the possible reversibility of the equation

$$ZnO + CO \rightleftarrows Zn + CO_2.$$
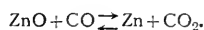
The experience of the zinc smelter proves that under certain conditions the reaction is a reversible one. When ores

containing the zinc as carbonate are smelted, instead of obtaining a compact mass of metal, the final product contains in some cases a variable amount of bluish powder. This blue powder is formed owing to the reaction

$$Zn + CO_2 = ZnO + CO$$
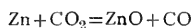
occurring under the given conditions of temperature and pressure, and the minute particles of zinc oxide become entangled with the volatilized zinc and prevent coalescence. Bondonard, however, has shown that if the amount of carbon dioxide does not exceed a certain low percentage the reverse reaction does not occur, and in such cases the zinc is obtained in a compact metallic form. A number of experiments were carried out under slightly varied conditions to determine how far the reduction of zinc oxide by carbon monoxide and weighing the resulting carbon dioxide could be relied upon as a qualitative test for zinc oxide. Different amounts of pure zinc oxide varying from 0.2 gramme to 0.02 gramme were weighed out into a porcelain boat which was introduced into the combustion tube, and a reduction carried out in a similar manner to the reduction of copper with carbon monoxide. With a slow current of gas flowing at the rate of one bubble per second, the amount of carbon dioxide formed corresponded to a much less weight of zinc oxide than was actually taken. When similar amounts of zinc oxide were taken but the rate of the current increased to three times the previous rate the amount of carbon dioxide formed corresponded to the actual weight of zinc oxide taken. The following are some typical results :—

Rate of Flow of Gas.	Temperature.	Amount of Zinc Oxide actually taken.	Amount of Zinc Oxide calculated from Carbon Monoxide formed.
		Gramme.	Gramme.
Slow	$900°$	0.2034	0.1512
do.	$1050°$	0.0209	0.0151
do.	$1050°$	0.1966	0.1645
Rapid	$1050°$	0.0219	0.0213
do.	$1050°$	0.1922	0.1904
do.	$1050°$	0.1938	0.1923

On examining the tube after an experiment in which low results were obtained, it was observed that the zinc had condensed in the form of a bluish powder, while in the experiments in which a rapid flow of gas had been maintained the zinc adhered to the tube in the form of clear metallic globules.

Further experiments were carried out with mixtures of copper and zinc. The copper had been ignited previously and the oxygen percentage determined, while the zinc used was that obtained as globules in previous experiments. The two metals were weighed out into a porcelain boat in the proportion of 10 grammes of copper to 3 grammes of zinc, and introduced into the combustion tube of the apparatus. The temperature of the furnace was kept at $1050°$ for two and a half hours, during which time a rapid current of carbon monoxide was passed. As the oxygen content of the copper was known, it was possible to calculate the amount of carbon dioxide compared with that obtained by experiment. The experimental and theoretical amounts of carbon dioxide were always in fair agreement, the former being slightly lower than the latter.

A number of tests were then carried out on samples of pure brass containing 60 to 70 per cent. of copper with negligible amounts of other metals. A piece of the alloy was taken, carefully filed, washed in alcohol, dried over quicklime, and introduced into the combustion pipe. The usual precautions were taken during the experiment; the carbon monoxide was passed in a rapid stream, and the furnace temperature quickly raised to $1050°$ and held there for at least one and a half hours. The absorption bulbs were weighed with the necessary precautions and the combustion prolonged for a further hour, though this was found to be unnecessary, as the bulbs remained constant in weight. After several preliminary experiments, it was found desirable to use a weight of metal not less than 30 grammes, otherwise the increase in weight of the absorption bulbs was so small as to come within the experimental error of the method. The weights of the brasses taken varied from 30 to 80 grammes, and in most cases the amount of carbon dioxide formed never corresponded to much above $0·002$ per cent. of oxygen, while in rare cases the amount

was negligible. The figures for a typical determination are given :—

A. *Blank Experiment.*

	Grammes.
Weight of absorption bulbs at commencement	$=82{\cdot}7732$
Weight of absorption bulbs after one hour's running at $1000°$ . . .	$=82{\cdot}7733$
Weight of absorption bulbs after two hours' running at $1000°$ . . .	$=82{\cdot}7732$

B. *Experiment with Brass.*

Weight of brass	$=49{\cdot}1030$
Weight of absorption bulbs at commencement	$=79{\cdot}9707$
Weight of absorption bulbs after passing steady current of gas without heating the furnace	$=79{\cdot}9707$
Weight of absorption bulbs after heating for one and a half hours at $1050°$ in a rapid current of gas	$=79{\cdot}9744$
Weight of absorption bulbs after heating for a further hour under similar conditions	$=79{\cdot}9746$
Increase in weight of absorption tube	$= 0{\cdot}0039$
Thus the weight of carbon dioxide formed	$= 0{\cdot}0039$

This weight of carbon dioxide gives the percentage of oxygen as

$$\frac{0{\cdot}0039 \times\ 4 \times 100}{11 \times 49 \times 1030} = 0{\cdot}0028.$$

This and similar results from other experiments prove that ordinary brasses of good quality contain on an average about $0{\cdot}002$ to $0{\cdot}003$ per cent. of oxygen, which is evenly distributed throughout the mass of metal, most probably in the form of very minute particles of oxide of zinc. When it is remembered that the specific gravity of metallic oxides is much less than that of the metal, it is easily understood that even this amount of oxygen in the form of oxide will occupy a greater bulk than is at first apparent. If any sample of brass gives, on reduction in carbon monoxide as previously described, a much higher figure than $0{\cdot}003$ per cent. of oxygen, then it is most probable that that particular portion contained an unusually large piece of zinc oxide or other oxide impurity which has become entangled during the casting. Further, the analysis of a specimen from one sample of brass may disclose a higher percentage of oxygen than another, and yet the latter may be found to corrode more rapidly than the former. This may be explained by the fact that the one will corrode more rapidly which contains the segregated pieces of oxides, as a greater difference in potential will be set up and the rate of corrosion will be more intense.

Some further tests were carried out with condenser-tube

brass containing about 2 per cent. of tin and German silver. In these cases, however, a rather surprising result was obtained, as a deposit of carbon was found adhering to the metallic surface after cooling down in an atmosphere of carbon monoxide. With the brasses this deposit was quite small, but the percentage of oxygen was on the average about 0.006 per cent. In the case of German silver, however, the deposit of carbon was quite a heavy one, and if the alloy were mixed with a small amount of tin the deposit was heavier still, while the oxygen percentage varied so much that it was evident there was decomposition of carbon monoxide occurring. Some zinc was melted alone in a current of carbon monoxide, as was also some tin, but in neither case did any decomposition of carbon occur. When, however, a mixture of tin and zinc was melted in the gas there was a deposition of carbon.

It would appear therefore from these experiments that while the percentage of oxygen in condenser tube brass containing only copper and zinc can be determined satisfactorily by ignition under carefully defined conditions in carbon monoxide, this method cannot be applied to the case of copper-zinc alloys containing either tin or nickel owing to the decomposition of carbon monoxide which is thereby caused.

In conclusion, the author wishes to thank Professor Carpenter, at whose suggestion this work was carried out, for his kindly interest and helpful advice tendered during the course of the work.

The research was carried out in the Metallurgical Laboratories of the University of Manchester.

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6. S. DICKSON, "Determination of Oxygen in Copper," *The Analyst,* vol. xxx. (1905) pp. 145–147.

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COMMUNICATION.

Mr. F. Johnson, M.Sc. (Birmingham), wrote that he expected to be able to test the efficiency of the author's method at no very distant date, and hoped that the difficulties which had formerly seemed insuperable in the determination of oxygen in brass had now been overcome.

Personally, he thought that the importance which was attached by many people to the existence of oxygen in brass had been over-rated.

On p. 371 the author made the following statement : " The presence of a certain amount of oxygen in copper, in proportions determined by the quantity of arsenic, is most beneficial." He (Mr. Johnson) would point out that that statement was a misleading one, since the amount of oxygen in arsenical copper was not necessarily determined by the quantity of arsenic, although affected by its presence.

In other words, 0·3 per cent. of arsenic, or 0·5 per cent., would in-fluence the proportion of oxygen as compared with the oxygen in pure copper, but there need be no difference in the amounts of oxygen in the 0·3 per cent. or 0·5 per cent. arsenical coppers.   Possibly a large increase of arsenic might enable the oxygen contents to be reduced, but in such a case one would not be dealing with commercial material.

He wished also to qualify the latter part of the statement, that oxygen was most beneficial.   That was perfectly true in the case of furnace-refined copper, where other impurities and gases had to be kept in check ; but, as he (Mr. Johnson) had shown in a paper * presented at the same meeting, the entire removal of oxygen from arsenical copper, in the pre-paration of which the purest materials had been used, could be attended with an all-round improvement in properties.

* Pages 275-93.

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By whom
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The following books have been purchased by the Institute :—

Twenty-eight volumes of the original communications to the Eighth International Congress of Applied Chemistry. (Washington and New York, 1912.)

Proceedings of the Association for Testing Materials, 1912 and 1913.

INSTITUTIONS.

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American Institute of Mining Engineers.
Chemical Society.
Concrete Institute.
Faraday Society.
Imperial Institute.
Institute of Marine Engineers.
Institution of Automobile Engineers.
Institution of Civil Engineers.
Institution of Electrical Engineers.
Institution of Engineers and Shipbuilders in Scotland.
Institution of Mechanical Engineers.

Institution of Mining and Metallurgy.
Institution of Naval Architects.
Iron and Steel Institute.
Junior Institution of Engineers.
Königliches Materialprüfungsamt.
North-East Coast Institution of Engineers and Shipbuilders.
Royal Society of Arts.
Society of Chemical Industry.
Staffordshire Iron and Steel Institute.
West of Scotland Iron and Steel Institute.
Washington, Department of Commerce and Labour.

JOURNALS.

The following periodicals are received regularly from their respective Editors :—

UNITED KINGDOM.

Chemical Trade Journal.
Civil Engineering.
Colliery Guardian.
Commercial Motor.
Engineer.
Engineering.
Hardware Trade Journal.
Hardwareman and Ironmongers' Chronicle.
Internal Combustion Engineering.
Iron and Coal Trades' Review.
Iron and Steel Trades' Journal.
Ironmonger.
Ironmongers' Weekly.
Machinery.
Marine Engineer.

Mechanical Engineer.
Metal Industry.
Mining Journal.
Mining Magazine.
Motor Cycling.
Motor Traction.
Motor Trader.
Nature.
Page's Weekly.
Railway Engineer.
Shipbuilder.
Steamship.
Tramway and Railway World.
Tramway and Railway World (Motor Traffic Section).

COLONIAL AND FOREIGN.

American Machinist.
Automobile.
Brass World.
Bulletin of the American Institute of Metals.
Canadian Machinery.
Canadian Mining Journal.
Castings.
Engineering and Mining Journal.

Journal of the Chemical, Metallurgical and Mining Society of South Africa.
Le Mois Minier et Metallurgique.
Metall und Erz.
Métaux et Alliages.
Motor Age.
Révue de Métallurgie.
South African Engineering.
Stahl und Eisen.
Steel and Metal Digest.

The Libraries of the following Institutions receive the Publications of the Institute free :—

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Birmingham University.
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Cambridge University.
British Museum.
Edinburgh University.

Glasgow University.
King's College, London.
Leeds University.
Manchester University.
National Library of Wales.
National Physical Laboratory.
Patent Office, London.
Sheffield University.
Trinity College, Dublin.

PRESENTATIONS TO THE MUSEUM

DURING THE YEAR 1913.

The following presentations to the Museum have been received and are gratefully acknowledged :—

Messrs. DURAM, LIMITED :

Case containing a bar of metallic tungsten, and two specimens of a similar bar after being hammered.

Four metallic tungsten electrical contact pieces.

A number of specimens of worked metallic tungsten.

Two tungsten springs.

Four cards of tungsten wire of 400, 500, 600, 700, 800, and 900 microns respectively.

Sample of tungsten in powder form.

Two samples of tungsten showing result of compression of the tungsten powder, and also finished metallic tungsten after heat treatment.

A case containing eight hard and soft spools of tungsten wire of 15, 20, 32, 43, 50, 65, 80, and 100 microns diameter respectively.

Messrs. MUNTZ'S METAL COMPANY, LIMITED :

A copper turning from the surface of a 10-inch copper billet for tube making. The turning is in one piece 12 feet long.

Mrs. G. SHAW SCOTT, B.Sc. :

Ten specimens of transparent metals, as follows :—

Aluminium heated to $400°$ C. for 1 hour.
Dutch metal.
Lead $\frac{1}{1600}$ inch thickness.
Lead heated up to $300°$ C. for 3 hours.
Lead heated up to $320°$ C.
Lead (unheated) $\frac{1}{1900}$ inch thickness.
Silver $\frac{1}{2850}$ inch thickness, heated to $400°$ C. for 30 minutes.
Silver heated to $360°$ C. for 35 minutes.
Silver heated to $400°$ C. in coal gas.
Silver heated to $405°$ C. for 29 minutes.

Mr. TOBIN :

Three specimens of nickel before and after heating, showing cracks resulting from heating.

Mr. STEPHEN VIVIAN (Messrs. The Dartmoor China Clay Company) :

Two portions of a corroded aluminium plate which has been in use on a cooling-floor for drying china clay.

LIST OF LANTERN SLIDES ON ELEMENTARY METALLOGRAPHY.

Presented by Mr. H. Garland (*Member*), Cairo, Egypt.

The Ideal Cooling Curve of a Solid Body.
Fusion Curve : Mixtures of Salt and Water.
Cast Lead : Structure.
Cast Silver : Structure.
Cast Copper : Structure.
Crystallites on the Cast Surface of Lead.
Crystallites in the Structure of an Old Bronze Statue.
Crystallites in the Structure of an Old Bronze Statue (another specimen).
The Fusion Curve of Lead-Antimony Alloys.
Lead-Antimony Alloy, with more than eutectic concentration of lead : Structure.
Lead Antimony Alloy : almost eutectic.
Zinc-Tin Alloy : 5 per cent. zinc.
Zinc-Tin Alloy : 15 per cent. zinc.
Magnesium-Tin Fusion Curve (Grube).
Copper-Zinc Equilibrium Diagram (in part).
Cast Brass, showing Cores.
Muntz Metal quenched above 750° C. homogeneous structure.
Same sample as cast and slowly cooled.
Muntz Metal extruded.
Silver-Copper Alloy : 40 per cent. silver.
Silver-Copper Alloy : nearly eutectic.
Brass : cold hammered.
Brass : cold hammered (larger view).
Brass : cold hammered (after annealing half an hour at 150° C.).
Same as above (larger view).
Same as above (after further annealing at 220° C.).
Same as above (larger view).
Brass : cold hammered (after further annealing half an hour at 450° C.).
Same as above, after annealing at a higher temperature (not recorded).
Same as above.
Same as above.
Recrystallization at the corner of cast brass, induced merely by the saw-cut and annealing.
Cuprous Oxide in Electrolytic Copper.
Cuprous Oxide in Commercial Copper.
Copper-Copper-Oxide eutectic.
Graphite in Cast Iron.
Mild Steel.
Grey Cast Iron.
Five per cent. Lead in Brass.
The Cooling Curve of an Alloy, 80 per cent. bismuth, 10 per cent. tin, 10 per cent. lead.
Structure of the above Alloy.
The Cooling Curve of the Alloy, 30 per cent. bismuth, 60 per cent. tin, 10 per cent. lead.
The Cooling Curve of the Bismuth-Tin-Lead eutectic.
The Structure of the above eutectic : at a low magnification, merely to show the apparent homogeneity of structure at low magnifications.

SECTION II.

ABSTRACTS OF PAPERS

RELATING TO THE NON-FERROUS METALS AND THE INDUSTRIES CONNECTED THEREWITH.

CONTENTS.

THE PROPERTIES OF METALS AND ALLOYS.

CONTENTS.

I.—*COMMON METALS.*

Action of Nitric Acid on Metals.—This subject has again been taken up by J. H. Stansbie.* The experiments indicate that the first reaction, in the case of copper, is the formation of a nitrite, which is then decomposed by the nitric acid. When the copper contains arsenic, the secondary reaction, in which ammonia is formed, becomes more prominent. In the copper-zinc series, the proportion of ammonia formed also increases with the zinc. Metallic bismuth behaves much like copper, and so does silver, except that less gas is formed.

Action of Sulphur Dioxide on Copper.—This reaction has been further examined by C. M. Stubbs.† Sieverts and Krumbhaar had found that sulphur dioxide, like hydrogen and other elementary gases, dissolves in molten copper proportionately to the square root of the pressure. Whilst this is the normal behaviour for an elementary gas, the behaviour of sulphur dioxide can only be accounted for by a reaction

$$6Cu + SO_2 \rightleftarrows Cu_2S + 2Cu_2O.$$
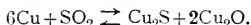
It is now found that the depression of the freezing point of copper by sulphur dioxide is 2·54 times as great as it would be if the molecules dissolved unchanged. Sievert's observation, that the equilibrium is affected by the addition of cuprous oxide or sulphide in the manner required by the above equation, is also confirmed. The equilibrium pressures have been determined from 700° to 1050°.

* *Journal of the Society of Chemical Industry*, 1913, vol. xxxii. p. 311.
† *Transactions of the Chemical Society*, 1913, vol. ciii. p. 1445.

Aluminium Foil.—Aluminium foil is now being used on a larger scale than ever before owing to improved methods of production and reduced cost.* It is partly displacing tin foil. According to *The Iron-monger*, the rolling is effected in six stages, the last of which yields a foil 0·04 millimetre (0·0016 inch) thick. The expansion in the use of extruded forms and tubing has been large during the last few years. Difficulties of this process have been largely surmounted, and metal of high tensile strength and compact structure is being turned out in almost any form called for.

Aluminium in Electrical Work.—Particulars are given † regarding the use of aluminium for electric cables.

Whilst the present annual output of copper is 1,004,485 tons, that of aluminium is given as about 60,000 tons, of which about 15 per cent. is used for electrical work. A very large increase in the production of aluminium is to be expected in the next two or three years. Commercial aluminium usually contains 0·5–0·7 per cent. of impurities, but it is stated that a maximum of 0·75 per cent. of impurities is permissible in aluminium required to compete with copper as a material for electrical cables.

Aluminium cables may be advantageously employed in positions near the sea or in sulphurous atmospheres, but are unreliable in localities where the air is charged with hydrochloric acid or alkaline vapours.

The higher coefficient of expansion of aluminium makes this metal compare unfavourably with copper from the present point of view, but this disadvantage is largely counterbalanced by the larger size, and consequently greater radiating surface of aluminium cables. The following table refers to the mechanical properties of individual wires of aluminium cables after stranding, and may be regarded as a specification basis for overhead cables :—

S. W. G.			Diameter of Wire, Inches.	Breaking Stress, Tons per Sq. Inch.	Extension of 5 Millimetres per Cent.
4	.	.	.	0·232	11·00	3·00
6	.	.	.	0·192	12·00	3·00
8	.	.	.	0·160	13·00	3·00
10	.	.	.	0·128	13·50	3·00
12	.	.	.	0·104	14·00	2·50
14	.	.	.	0·080	14·50	2·50
16	.	.	.	0·064	14·75	2·50

The breaking loads given above closely follow the values obtained by the relation

$$T = 16·5 - 24D.$$

where T = tensile strength in tons per square inch and
D = diameter of wire in inches.

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* *Engineer*, 1913, vol. cxvi. p. 199.   † *Engineering*, 1913, vol. xcv. p. 812.

A wrapping test is also adopted to ensure against brittleness in the wires. The elastic limit should be about 70 per cent. of the breaking strain in every case. A number of examples from actual practice are given, showing how aluminium compares with copper as a cable material both for insulated underground conductors and for bare overhead transmission, and from an economic standpoint the results quoted often show figures favouring the lighter metal. It is stated that on the Continent there are about 800 miles of aluminium cable at present in use, transmitting current at pressures varying from 240 to 60,000 volts.

Experiments by the British Insulated and Helsby Cable Company, Limited, on the stress-strain relations for aluminium wire are briefly described,* and the following figures are given :—

Diameter	0·457 inch.
Area	0·0193 sq. inch.
Length	7·56 inches.
Maximum stress	29,000 lb. per sq. inch.
Yield point	23,800 ,, ,,
Elastic limit	20,700 ,, ,,
Elongation	4·1 per cent. (on 7·56 inches).

A feature of the tests is the well-marked limit of elasticity.

Aluminium Solder.—An alloy consisting of tin 38, phosphor-tin 32, and zinc 30 per cent. is claimed by R. Seifert to be effective in soldering aluminium to aluminium or to brass and bronze. The alloy has been patented.†

Arsenical Copper and the Brass Industry.—In discussing the advisability of employing arsenical copper for the manufacture of high-grade rolled brass, E. A. Lewis ‡ severely criticizes the American Standard Copper Specifications.§ It is pointed out that the Birmingham brass manufacturer, employing mixtures of arsenical and electrolytic coppers, can turn out brass of a quality at least equal to that obtained in America, where electrolytic copper is more largely used. Results are given of a series of tensile tests on brasses made from both arsenical and electrolytic copper. Tensile test-bars of the various alloys were prepared both in the cold-rolled and annealed conditions. The composition of the various alloys and the results of tensile tests on the annealed bars are given in the table on p. 395.

Results obtained with the same alloys in the hard-rolled condition are also given. It may be pointed out that in the table three of the arsenical alloys show a higher tensile strength and elongation than the corresponding brasses made from electrolytic copper. The author concludes that a proportion of about 0·06 per cent. arsenic in brass is entirely beneficial, rendering the metal more fluid and increasing the ductility of the solid material. For gun-metal castings it is stated that

* *Engineering*, 1913, xcvi. p. 197.
† *Metallurgical and Chemical Engineering*, 1913, No. 4, vol. xi. p. 197.
‡ *Metal Industry*, 1913, vol. v. p. 96.
§ See also *Journal of the Institute of Metals*, 1912, No. 2, vol. viii. p. 317.

Alloy No.	Copper.	Arsenic.	Reduction of Area.	Tensile Strength, Lb. per Sq. Inch.	Elongation on 4 Inches.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
1	61·44	0·065	54·1	50,200	43·50
2	67·43	0·068	61·2	44,700	61·00
3	69·97	0·068	62·75	44,000	60·00
4	74·60	0·068	61·50	44,100	57·75
5	61·90	nil	55·85	49,450	48·25
6	67·01	nil	60·45	43,770	57·50
7	69·52	nil	61·15	43,600	57·75
8	74·56	nil	60·90	44,125	58·75

arsenical copper containing as much as 0·5 per cent. arsenic may be usefully employed. In this connection see also paper by F. Johnson, on p. 275.

Boronized Copper.—A further description of the method of casting conductivity copper deoxidized by boron suboxide, is given by R. D. Thomson * of the General Electric Company, New York.

It is stated that in casting this material larger risers and gates must be employed than are usual in the case of ordinary copper, as the shrinkage is greater in the case of boronized copper. With this exception, the process does not differ greatly from the casting of ordinary copper and brass.

A minimum of 1 per cent. of boron suboxide is added to the copper. Additions in excess of this amount are not injurious, since, unlike other deoxidizers, the suboxide does not combine chemically with the copper.

The following figures are given for the mechanical properties of the material :—

Tensile strength, 24,350 lb. per square inch ; elastic limit, 11,450 lb. per square inch ; reduction of area, 74·49 per cent. An electrical conductivity of 90 per cent. is given as an average figure for this class of material. Photographs are shown indicating the various applications of the method in making electrical fittings.

Deoxidation of Copper.—Experiments have been carried out by F. Hüser † with a view to investigating the relative value of various metals and non-metals as deoxidizing agents for copper. The comparative experiments show that the best quality of copper, especially as regards electrical conductivity, is obtained by the use of magnesium.

Quantities of 6–10 kilogrammes of copper were melted for each experiment. The deoxidizing agents used were tin, zinc, nickel, iron, manganese, silicon, chromium, boron, phosphorus, aluminium, and magnesium. The following results are given :—

* *Metal Industry*, 1913, vol. v. p. 101.
† *Metallurgical and Chemical Engineering*, 1913, No. 9, vol. xi. pp. 518–520.

	Tin.	Zinc.	Nickel.	Iron.	Manganese.	Silicon.	Chromium.	Boron.	Phosphorus.	Aluminium.	Magnesium.			Starting Material.
Refining material added (per cent.	0·4	0·4	0·2	0·2	0·2	0·2	0·15	0·1	0·1	0·1	0·1	0·1	0·1	...
Refining material found (per cent.)	0·37	0·35	0·18	0·16	0·13	0·17	0·04	...	0·07	0·09	0·013	0·024	0·039	...
Electrical conductivity in per cent. of that of purest copper (100–60)	73·0	73·0	79·1	58·8	70·5	55·3	91·0	83·8	62·1	83·8	98·5	94·0	89·1	97·1
Breaking stress (kilogrammes per square millimetre)	50·1	44·5	40·8	45·5	43·3	42·6	39·3	42·6	44·4	41·7	42·9	41·4	41·9	42·8
Elongation (per cent.)	3·5	3·0	2·0	3·5	3·0	3·0	0·3	3·0	2·5	3·0	2·75	2·0	3·0	2·0
Number of twists (radius of 100 millimetres)	7	8	8·5	6·5	7	7	7	8	8·5	7	8	7·5	6	5·5

The above tests relate to material rolled into bars 8 millimetres diameter and then drawn to 5 millimetres diameter without subsequent annealing. The cast copper purified with magnesium has a breaking stress of 18·5–21 kilogrammes per square millimetre, with an elongation of 30–37 per cent., is very ductile, and can be rolled into very thin sheets without tearing at the edges. Magnesium was most conveniently added in the form of copper-magnesium alloy, containing 20 per cent. magnesium, which is quite brittle. A bisilicate slag (FeO, CaO, $2SiO_2$) was used and found very suitable for absorbing resulting oxide. Photographs of sections of billets treated and untreated are given. Cuprous ammonium-chloride solution was used as etching reagent.

Effect of Impurities on the Rolling of Zinc.—Starting with a rather impure spelter, E. Prost and A. van de Casteele * find, using ingots of about 40 lb., that lead does not interfere with the rolling qualities when below 1·25 per cent., but that any increase above this is injurious. Cadmium is injurious if above 0·25 per cent., whilst arsenic and antimony are harmful from 0·02 per cent. upwards, arsenic in particular having a very great hardening effect. As little as 0·01 per cent. of tin has a bad effect. Copper below 0·08 per cent. has no effect, or iron below 0·12 per cent.

Effect of Sulphur on Copper.—In a paper describing some experiments on the effect of sulphur on copper, E. S. Sperry † suggests that the injurious effect of sulphur on copper, brasses and bronzes has been much underestimated, and he proposes to include sulphur amongst the constituents which should always be determined in a complete analysis of these materials.

* *Bulletin de la Société Chimique de Belge*, 1913, vol. xxvii. p. 175.
† *Brass World*, 1913, vol. ix. p. 91.

Samples of copper containing varying amounts of sulphur were obtained by adding lump sulphur to the molten metal.

Two experiments, in which a large excess of sulphur was added, gave a copper containing only 1·06 and 1·04 per cent. of sulphur. This appears to be the saturation concentration. The excess of sulphur separated out and formed a black scale of cuprous sulphide covering the outside of the ingot. This highly sulphurous metal was quite fluid, but when solidified it was found to be extremely brittle, the fracture showing many blowholes.

A copper containing 0·89 per cent. of sulphur was found to have forging properties which appeared quite normal at high temperatures, but the metal showed brittleness when forged at a dull red heat. With 0·10 − 0·53 per cent. of sulphur, copper was found to be fairly malleable but still very brittle under bending forces. [The author appears to be surprised at this apparent discrepancy in the strength of his samples, but it may be suggested that the effect could be readily accounted for by the very large number of blowholes which were found in the interiors of all the specimens.—*Note by Abstractor.*]

In advocating the use of scrap copper wire in the brass foundry, it is pointed out * that since the wire is of conductivity quality it must necessarily be of such purity that it may be employed advantageously in foundry work. An interesting point with regard to the various kinds of copper-wire scrap is that, whereas wire which has been insulated by cotton and wax may always be regarded as safe for brass-making purposes, it has been found that rubber-insulated wire often becomes brittle on burning off the insulation : this is attributed to the absorption of sulphur from the rubber by the heated metal.

Explosion in Granulating Aluminium.—An explosion is described by M. Bamberger and H. von Jüptner † as taking place during the pouring of molten aluminium through a sieve into water for granulation for use in steel. A slight explosion was followed by a violent one, which was fatal to two men. The second one must have been due to the mass of metal falling into the water. The sieve used was a perforated graphite crucible, and it is suggested that this cracked, and allowed its contents to fall, or that it was moist, and so caused a steam explosion.

A. Hempel ‡ attributes the explosion to the formation of steam, and suggests that the workmen, alarmed by the small explosion, which explosions are also common in granulating copper, allowed the crucible or its contents to fall into the water.

Impurities in Muntz Metal.—The influence of varying amounts of antimony, arsenic, and bismuth on Muntz metal has been investigated by F. Johnson.§

Some brands of copper have been found to give Muntz metal of normal

* *Brass World*, 1913, vol. ix. p. 57.
† *Zeitschrift für angewandte Chemie*, 1913, vol. xxvi. p. 353.
‡ *Ibid.*, p. 464.
§ *Engineering*, 1913, vol. xcv. p. 283.

quality, whilst other brands of copper, of very similar quality as to purity, yield a Muntz metal which is very brittle and has a coarsely crystalline structure. To investigate this phenomenon, a number of alloys were made containing arsenic, antimony, and bismuth, these impurities being added either singly or two at a time. The basis metals were pure electrolytic copper and commercial zinc. Since the latter metal contained known amounts of lead and iron, the conditions of experiment were similar to those obtaining in practice. The following is an analysis of the normal alloy :—

								Per Cent.
Copper	.	.	.	.	.	.	.	60·83
Zinc .	.	.	.	.	.	.	.	38·64
Lead	.	.	.	.	.	.	.	0·45
Iron .	.	.	.	.	.	.	.	0·08

and to this antimony, arsenic, and bismuth were added as desired.

Two ingots of each alloy were cast, one having a fine structure (chill cast) and the other being cooled more slowly. The ingots were then reduced by 60 per cent. of their original thickness by forging hot, and were finally thinned down a further 34 per cent. by a number of alternate cold rolling and annealing processes. Thus the effect of the various impurities on both the hot-working and cold-working qualities of the alloys were examined.

When only one of the three impurities was added it was found that 0·6 per cent. of antimony rendered the Muntz metal coarsely crystalline and rotten under both hot and cold work, whilst 0·61 per cent. of arsenic or 0·31 per cent. of bismuth had a slightly injurious effect on the hot-working qualities only.

When, however, the impurities were added two at a time a combination of only 0·04 per cent. of antimony and 0·04 per cent. of arsenic was sufficient to render the Muntz metal quite brittle under the hot-work test, the fracture being coarsely crystalline. In cold rolling, however, this alloy appears to have behaved very similarly to the pure Muntz metal.

A micrograph of this impure alloy is given, and shows that the presence of the antimony and arsenic tends to increase the amount of β-constituent as compared with a photograph showing the structure of the pure Muntz metal.

Passivity of Metals.—Further work on passivity by N. Isgarischeff * leads to the conclusion that soluble peroxides are formed as intermediate stages in the production of passive nickel, cobalt, iron, and cadmium. In these cases, in alcoholic solutions of their salts, the passivity is certainly to be attributed to the formation of films of oxide. In other cases, as in that of copper in cupric chloride in alcohol, the formation of complex salts intervenes.

* *Zeitschrift für Elektrochemie*, 1913, vol. xix. p. 491.

II.—*RARE METALS.*

Barium Preparation.—It has been found by C. Matignon * that barium may be reduced from its oxide by silicon or ferro-silicon, although the heat of formation of silica is inferior to that of baryta. By using an excess of baryta, barium silicate is formed with development of heat, and the quantity of heat to be supplied from the outside is thus reduced. At about 1200° a mixture of baryta with pure silicon or 90 per cent. ferro-silicon, the latter being preferable on account of its brittleness and cheapness, gives a smooth reaction, and barium containing 98·5 per cent. of the metal is readily obtained as a distillate. Electrical heating is advantageous.

In the same manner magnesia may be reduced by aluminium,† provided that an excess of magnesia is used and the mixture is heated to 1200° in an exhausted steel tube. Magnesium aluminate is formed, and magnesium sublimes in crystals.

Beryllium.—The properties of metallic beryllium have been described by F. Fichter and K. Jablczynski.‡ The metal is best prepared by electrolyzing a mixture of sodium fluoride (1 mol.) and beryllium fluoride (2 mols.) in a nickel crucible. If too strongly heated, an alloy of nickel and beryllium is formed. The metal is obtained in good crystals, with a current efficiency of 33 per cent. The crystals are mixed with a little oxide, which may be removed by centrifuging with a mixture of ethylene bromide and alcohol, of specific gravity 1·95. The product then contains 98 per cent. of the metal. It is not possible to obtain compact metal by simple fusion, as beryllium becomes coated with a thin, very adherent layer of oxide. If the crystals are compressed into cylinders, they may be fused in a tungsten vacuum furnace, yielding small ingots, which cannot be united by fusion, owing to the formation of oxide films. A temperature of 1500° is necessary, although the actual melting-point is only $1280° \pm 20°$, as determined by an optical pyrometer in a tungsten furnace. The fused beryllium contains only traces of impurities; it has specific gravity 1·842, and hardness between 6 and 7. It is brittle when cold, but becomes ductile at a red heat. The electrical conductivity is one-twelfth that of copper. The surface is oxidised by water, but the action is soon stopped by the formation of a protecting layer. Beryllium anodes show the same valve-action as aluminium. In its resistance to acids it stands between magnesium and aluminium.

Ductile Tungsten.—A history of the preparation of ductile tungsten is given by N. L. Müller. § The first method (1903) was that of heating a carbon filament in an atmosphere of tungsten oxychloride and hydrogen :

$$WOCl_4 + C + 2H_2 = 4HCl + CO + W.$$
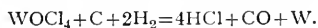
* *Comptes Rendus*, 1913, vol. clvi. p. 1378.   † *Ibid.*, p. 1157.
‡ *Berichte der deutschen chemischen Gesellschaft*, 1913, vol. xlvi. p. 1604.
§ *Zeitschrift für angewandte Chemie*, 1913, vol. xxvi. pp. 404, 422.

Next followed the squirting method, organic substances being used to convert the powdered metal into a paste, which was then squirted into threads and heated in a reducing atmosphere. The colloid process depends on the preparation of a colloidal suspension of tungsten, which is then coagulated and forms a tough binding mass for mixing with tungsten powder. The present method is mechanical, and follows that used in preparing other ductile metals, with the difference that it is necessary to hammer the metal at a high temperature in a reducing atmosphere.

Ductile tungsten has a specific gravity 19·6–20·2, a tensile strength reaching 420 kilograms per square millimetre, a coefficient of expansion about one-half that of platinum, and an electrical resistance of 6·2 micro-ohms per cubic centimetre.

Osmium.—The recovery of osmium from residues containing organic matter, according to A. Gutbier,* is best accomplished by heating in a current of oxygen, which removes carbon and converts the metal into the volatile tetroxide, which is distilled into an alcoholic solution of hydrazine hydrate. The reduced metal is heated in hydrogen.

Palladium and Hydrogen.—Experiments by A. Gutbier, H. Gebhardt, and B. Ottenstein † show that spongy palladium, prepared in an atmosphere of carbon monoxide, absorbs more hydrogen as the temperature falls below zero. The curve of absorption has a well-marked minimum at $+20°$. The palladium saturated with hydrogen is pyrophoric.

Vanadium.—Particulars of vanadium ores and their treatment are given by H. Manz.‡

Precipitated vanadic acid, containing 90–95 per cent. of V_2O_5, or ferrous vanadate is the usual end-product of the treatment of the ore. The principal product required is ferro-vanadium, free from carbon, and this is prepared by the alumino-thermic process from vanadic acid, hammer scale and aluminium in iron vessels lined with magnesite. The best product contains about 33 per cent. of vanadium, but from 25 to 55 per cent. may be found. The pure metal has not found application on account of its cost and its high melting point ($1715°$). It may be obtained by the alumino-thermic process.

Other commercial alloys are cupro-vanadium with 3 per cent. V, nickel-vanadium with 18–25 per cent. V, aluminium bronze with 0·5 per cent. V and 5 per cent. Al, and manganese bronze with 0·03 per cent. V. At present prices, 25 per cent. ferro-vanadium costs about 5s. a pound. The American consumption in 1911 amounted to 1130 metric tons, almost entirely for steel manufacture.

* *Chemiker Zeitung*, 1913, vol. xxxvii. p. 857.
† *Berichte der deutschen chemischen Gesellschaft*, 1913, vol. xlvi. p. 1453.
‡ *Metall und Erz*, 1913, vol. x. p. 379.

III.—*ALLOYS.*

Aluminium-Tin Bronzes.—The microstructure of special bronzes of aluminium and tin and of ternary alloys containing zinc, aluminium or tin, silicon, antimony, and arsenic, has been studied by F. Robin.* Two types of microstructure consisting of interlocking needles are found, one typical of material which has been subject to prolonged annealing known as Widmanstätten, and the other martensitic and characteristic of quenched solid solutions. The hardening, tempering, and annealing of the alloys has been studied with a view to the determination of the conditions under which the martensitic structure is produced and destroyed. The size of the needles obtained on quenching aluminium alloys increases with aluminium content up to about 14 per cent. If such an alloy is quenched from 1000° C., and afterwards tempered at various temperatures, it is possible to obtain the sorbitic, granular, and pearlitic structures characteristic of steel. The structure similar to austenite cannot be obtained. Local production of the Widmanstätten structure is obtained by prolonged annealing at 1000° C. The production of the martensitic structure in tin bronzes is not so easy, but can be obtained by quenching a 25 per cent. alloy from just below the solidus. A structure similar to austenite can be obtained by quenching from the freezing point. Much more rapid tempering takes place than in the case of the aluminium alloys. The metallographic equivalence of the various metals is discussed. The paper is illustrated with photomicrographs.

Cadmium Arsenides.—The compounds of cadmium and arsenic have been examined by S. F. Schemtschuschny.† The alloys are best prepared by melting cadmium under a layer of potassium and lithium chlorides, and adding coarsely broken arsenic. In this way there is very little loss of arsenic.

The freezing point curve has a very pronounced maximum at 721° C., corresponding with the compound Cd_3As_2. There is a second maximum at 621° C., corresponding with $CdAs_2$, but, as in the cadmium-antimony series, the formation of this compound is readily suppressed by undercooling, and it does not crystallize unless the melt is inoculated with the proper crystals. Failing inoculation, the descending branch of the Cd_3As_2 curve is much prolonged, reaching a metastable eutectic point at about 526° C., instead of the stable eutectic at 610° C. The structure and properties of these alloys are therefore very different, according as the melt is inoculated or not. The compound Cd_3As_2 undergoes a polymorphic change at 578° C. Solid solutions are not formed, and there is no compound between $CdAs_2$ and arsenic.

The specific gravity and atomic volume curves show well-marked breaks corresponding with the two compounds, both of which are formed from their components with expansion, the specific gravities being—Cd_3As_2,

* *Bulletin de la Société d'Encouragement*, 1913, vol. cxix. pp. 12–41.
† *Internationale Zeitschrift für Metallographie*, 1913, vol. iv. p. 228.

$6 \cdot 25$; and $CdAs_2$, $5 \cdot 86$. The latter compound is harder than either component. The first compound is dark grey, with a reddish shade, and the second very dark grey, with a bluish shade.

Calcium Boride.—A convenient method of preparing calcium boride is described by E. Wedekind.* Calcium borate is mixed with calcium turnings and heated to dull redness in an iron bomb, when the reaction sets in. The product is crushed and extracted first with dilute acetic acid, and then with warm dilute hydrochloric acid.

Calcium boride is a light brown, micro-crystalline powder of specific gravity, $2 \cdot 11$ at $18°$. When pressed it forms compact masses, which conduct electricity. The composition corresponds with the formula CaB_6. When heated electrically, it sinters, and yields a compact mass of greater hardness than corundum. It resists the action of acids, except nitric, and of alkaline solutions, but is readily attacked by fused alkalies. It oxidizes slowly, with superficial incandescence, when heated in air. Unlike either calcium or boron, it is not altered by heating in nitrogen.

Casting Temperature for Aluminium Alloys.—The effect of variations in pouring temperature on the strength of a large number of aluminium alloys has been investigated by H. W. Gillett.†

Since the strength of a given alloy is largely dependent on size of crystal grain, it is of primary importance to obtain the cast material with the correct structure, and the desired closeness of the grain is obtained in practice by casting at a suitable temperature.

Preliminary investigations as to the nature and dimensions of the test-bars showed that the gain in accuracy obtained when using bars machined true over the breaking section, and made with threaded ends for screw grips, was not sufficient to justify the extra labour involved ; the difference in tensile strength between a bar as sand-cast and a bar of the same alloy carefully machined and threaded being of the order of only 600 lb. per square inch. The tests enumerated were therefore made on sand-cast bars broken in wedge grips.

With regard to the dimensions of the bar, it was found that, using a round bar of a certain copper-aluminium alloy, an increase in diameter of $0 \cdot 6''$ (from $0 \cdot 4'' - 1 \cdot 0''$) caused a drop in tensile strength of 6500 lb. It was therefore decided to use a standard size of bar with a breaking section $2''$ long by $\frac{1}{2}''$ diameter. Results are given in the paper comprising the averages of tests on over fifty alloys of aluminium with varying quantities of one or more other metals. These include, amongst others, the following :—

* *Berichte der deutschen chemischen Gesellschaft*, 1913, vol. xlvi. p. 1885.
† *Metal Industry*, 1913, vol. v. p. 193.

No.	Composition.	Pouring Tempera- ture, Degrees F.	Tensile Strength, Lb. per Sq. In.	Pouring Tempera- ture, Degrees F.	Tensile Strength, Lb. per Sq. In.
1	Commercially pure Aluminium .	1,400	10,500	1,600	8,000
5	Aluminium plus 8 per cent. copper	1,225	20,000	1,600	15,500
11	,, ,, 16 per cent. zinc	1,225	24,000	1,550	17,000
15	,, ,, 32 per cent. zinc.	1,225	35,000	1,550	30,000
30	{ Aluminium plus 3 per cent. cop- per, 15 per cent. zinc, ½ per cent. manganese . .	1,225	30,000	1,550	20,000
31	{ Aluminium plus 2½ per cent. cop- per, 19 per cent. zinc .	1,225	33,000	1,550	25,000
35	{ Aluminium plus 1¾ per cent. copper, 30 per cent. zinc .	1,225	42,000	1,550	34,000
37	{ Aluminium plus 2 per cent. man- ganese . . .	1,200	19,000	1,550	18,500
43	{ Aluminium plus 5 per cent. copper, 3 per cent. tin .	1,215	16,800	1,500	15,000
44	{ Aluminium plus 6 per cent. cop- per, 1 per cent. nickel .	1,300	18,200	1,600	14,500
53	{ Aluminium plus 5 per cent. mag- nesium	1,250	20,500	1,400	20,000

It is pointed out that, except in the cases of alloys Nos. 37 and 53, the hot-cast bars are usually about 20 per cent. weaker than those cast at the lower temperatures.

The author concludes with a criticism of the results published by other workers on aluminium alloys, and advocates the use of a base metal couple for taking casting temperatures of such alloys.

Cobalt-Chromium Alloys.—The economic applications of alloys of cobalt and chromium containing other elements are discussed by E. Haynes,* and some remarkable mechanical and chemical properties are claimed for these alloys, more particularly when they contain tungsten and molybdenum, either singly or in combination.

The effect of tungsten on a cobalt-chromium alloy was investigated ; the proportion of chromium was kept constant at 15 per cent., and gradually increasing additions of tungsten were made, the proportion of cobalt present suffering corresponding decreases. It was found that the characteristic effect of tungsten is to increase the hardness of the alloy, at the same time reducing the malleability. Alloys containing up to 10 per cent. tungsten are said to forge readily, but from this point the malleability falls off rapidly, and with 25 per cent. of tungsten the alloys are very brittle and hard, and are said to possess advantages over steel as a material for high-speed cutting tools.

An alloy containing 40 per cent. of tungsten is recommended for turning cast iron, and it is stated that, using a small drill made of this alloy, holes were easily driven through thick bottle glass, without the aid of any liquid or lubricant. The effect of molybdenum on cobalt-

* *Brass World*, 1913, vol. ix. p. 21.

chromium alloys was found to be similar to that of tungsten. It is said that all these alloys have a high resistance to oxidation and corrosion.

A further communication on this subject * gives particulars of the composition and properties of these alloys, which may conveniently be tabulated as below :—

Cobalt.	Chromium.	Tungsten.	Molyb-denum.	Properties.
Per Cent.	Per Cent.	Per Cent.	Per Cent.	
75	25	...	...	Original "Stellite" alloy.
70	25	5	...	Forges readily at red heat and takes a good cutting edge. Very non-corrosive. Suitable for wood-working tools and cutlery.
60	15	25	...	Lathe tools for cutting steel or cast iron.
55	15	25	5	High-speed cutting tools. Said to increase speed of cutting 50–100 per cent. as compared with best grades of high-speed steel.
45	15	...	40	Very hard. Cuts glass easily and will even scratch quartz.

The alloys have been patented by the inventor.

In commenting on the use of Stellite alloys for cutting tools, A. R. Ledoux gives some interesting figures as the results of tests by an independent worker, which go to show that, in machining phosphor-bronze, tool steel, mild steel, and cast iron, the work can be put through from two to four times as rapidly when using Stellite as when a good grade of high-speed steel is employed.

Cobalt-Nickel Arsenides.—A thermal analysis by K. Friedrich † deals with the system Co—CoAs, which gives indications of compounds Co_5As_2, Co_3As_2, and Co_2As, and with the system Ni—NiAs, which gives the compounds Ni_5As_2, and probably also Ni_3As_2. The study of the ternary mixtures makes it certain that a compound Ni_2As does not exist under the given conditions. The liquidus surfaces of the ternary system have been determined.

Copper-Aluminium Alloys.—The structure of the alloys of this series, containing from 84 to 90 per cent. of copper, has been studied by H. Hanemann and P. Merica.‡ The alloys crystallize very rapidly during cooling. If cooled very slowly, both a and γ form large plates, with a lamellar eutectoid between them. With more rapid cooling, the γ constituent forms crystallites, whilst both a and the eutectoid tend

* *Brass World*, 1913, vol. ix. p. 159.
† *Metall und Erz*, 1913, vol. x. p. 659.
‡ *Internationale Zeitschrift für Metallographie*, 1913, vol. iv. p. 209.

to form needles. These needles are still more conspicuous on quenching. The author takes the view that these needles represent a true dissociation of the solid solution, and not a mere twinning structure. A close analogy exists between these alloys and the steels. The needle structure corresponds with martensite, and undecomposed β, which may be obtained by rapid quenching, represents austenite. The γ crystals correspond with cementite.

The decomposition of the β constituent has been studied in more detail by A. Portevin.[*] The eutectoid occurs in two forms, one granular and comparatively coarse, the other finely laminated. The latter type is never found in immediate contact with α crystals, but may occur in the pure eutectoid or in contact with γ crystals. It very closely resembles pearlite. It is pointed out that these two types of eutectic structure are also met with in other alloys, such as those of copper and antimony. In a note to this paper, W. Guertler [†] remarks that similar differences are observed in the eutectic of white iron, the differences being mainly due to the cutting of the network at varying angles.

Effect of Remelting on the Strength of Gun-metal.—Results are given [‡] of some experiments conducted to investigate the effect of remelting on gun-metal.

The alloy employed was a Government bronze containing :—

								Per Cent.
Copper	.	.	.	.	.	.	.	87·57
Tin	.	.	.	.	.	.	.	10·54
Zinc	.	.	.	.	.	.	.	1·82
Lead	.	.	.	.	.	.	.	0·04
Iron	.	.	.	.	.	.	.	0·03

The copper, tin, and zinc were alloyed together in the usual way, and cast into test-bars in green sand moulds. The test-bars were machined to a diameter of 0·75 inches over a length of 10 inches. The effect of remelting is shown in the following :—

No.		Tensile Strength, lb. per Sq. Inch.	Elongation on 8 Inches.	Reduction of Area.
			Per Cent.	Per Cent.
1	After first melt . .	28,800	10·2	10·6
2	Melted twice . .	34,800	15·5	14·2
3	Melted twice . .	39,000	17·0	20·4

Numbers 2 and 3 were poured at different temperatures.

and it will be seen that the effect of remelting is to make the material stronger and yet more ductile. Analyses of the test-bars after the

* *Internationale Zeitschrift für Metallographie*, 1913, vol. iv. p. 257.
† *Ibid.*, p. 261.   ‡ *Brass World*, 1913, vol. ix. p. 176.

various meltings showed that the composition had not altered in the least, and on the evidence of the fractures the difference in mechanical properties is ascribed to the elimination of blowholes and the production of a fine-grained structure by remelting.

Lead-Copper Alloys.—As the first part of an investigation of systems containing two liquid layers, K. Friedrich * publishes an account of the alloys of lead and copper. The original apparatus of Spring and Romanoff was improved by using an electric furnace in place of gas, by stirring the molten alloy mechanically, and by using fine silica pipettes for the removal of the liquid for analysis. Porcelain crucibles were used, taking 300 grammes of alloy, stirred by a porcelain propeller. After stirring for an hour the mixture was allowed to remain at constant temperature for fifteen hours before withdrawing the samples. Under these conditions liquid alloys of lead and copper become homogeneous at 1025° C., but when only a short time is allowed for attaining equilibrium the temperature at which the two layers become one is as high as 1300° C. The range of composition within which separation into two layers takes place at 953° C. is rather narrower than that found by Heycock and Neville, the limits now found being 19 and 54 per cent. of copper. The thermal method in such a case is less accurate than the solubility method, on account of the long time required for the attainment of equilibrium, and the smallness of the thermal effect.

Manganese-Silver Alloys.—A thermal study by A. Arrivant † gives a compound, Ag_2Mn, melting at 980° C., which forms a continuous series of solid solutions with silver, this part of the curve passing through a minimum at 955° C. Between 94 and 31 per cent. of manganese, the alloys form two liquid layers. The electromotive force shows a sharp break at the composition Ag_2Mn, with a gradually sloping curve on the silver side of this point. The compound may be isolated from alloys rich in manganese by treatment with dilute acids, and is then obtained as a glistening powder, stable towards even concentrated nitric or sulphuric acid in the cold.

Metallic Borides.—The preparation of metallic borides has been advanced by the work of E. Wedekind.‡ A vacuum furnace is used, and an arc is produced between two rods composed of a mixture of the finely divided metal with amorphous boron. This mixture is consolidated by a pressure of several hundred atmospheres, and the rods are made to conduct sufficiently by sintering before the application of the arc. The product collects in a crucible placed beneath the arc in the form of small globules.

Zirconium boride, Zr_3B_4, is stable in air, has a hardness of 7, and a specific gravity 5. Vanadium boride, VB, and uranium boride, UB_2,

* *Metall und Erz*, 1913, vol. x. p. 575.
† *Comptes Rendus*, 1913, vol. clvi. p. 1539.
‡ *Berichte der deutschen chemischen Gesellschaft*, 1913, vol. xlvi. p. 1198.

are very similar in properties. Tungsten boride, WB_2, has the high specific gravity 10·7. It was not found possible to obtain a pure molybdenum boride. In the light of modern knowledge of alloys, it must not be assumed as certain that the substances thus obtained are definite compounds.

Molybdenum and Tungsten Carbides.—Both molybdenum and tungsten have been converted into their carbides by S. Hilpert and M. Ornstein * by acting on the powdered metal with methane or carbon monoxide. Thus molybdenum and carbon monoxide yield a definite carbide, Mo_2C, at 800° C. With prolonged action of the gas a higher carbide is obtained, but equilibrium is reached very slowly and the formula of the resulting carbide is uncertain. Large crystals of the carbide Mo_2C are obtained by reducing the trioxide in carbon monoxide, but these crystals, sometimes 1 millimetre long, may possibly be pseudomorphous after the oxide.

With tungsten, the maximum carburization is not reached below 1000° C., at which temperature the formula W_3C_4 is approached. Reduction of the trioxide yields the metal and not the carbide. A mixture of methane and hydrogen rapidly converts tungsten into the carbide WC at 800° C. These carbides are metallic in character.

Platinum-Osmium Alloys.—F. Zimmermann † has found that osmium may be alloyed with platinum in place of iridium, and that smaller quantities of osmium than of iridium are required to give alloys having equal hardness and similar electrical properties.

Resistance of Nickel-Cobalt Alloys.—These alloys have been examined in the cast condition by R. Ruer and K. Kaneko.‡ The maximum resistance and minimum conductivity occur at about 17 per cent. of cobalt, the curve being very steep on the nickel side and practically linear on the cobalt side. The hardness by Brinell's test is very irregular in the cast condition, but becomes uniform after heating to 1150° C. The hardness curve has then a peculiar form, being nearly horizontal from 0 to 60 per cent. of cobalt, then rising very steeply and passing through a maximum at 92 per cent. of cobalt. The same discontinuity at about 70 per cent. was observed by these authors in the magnetic properties and in the micrographic structure, the lamellar twinning of the polygonal grains only being observed from 70 per cent. upwards.

Soft Solder.—An alloy containing, approximately, tin 41·5, phosphorus 0·02, antimony 2 per cent., and the balance lead has been patented by J. T. Dwyer § as being cheaper than, and superior to, the soft solder in present use.

* *Berichte der deutschen chemischen Gesellschaft*, 1913, vol. xlvi. p. 1659.
† *Metallurgical and Chemical Engineering*, 1913, No. 7, vol. xi. p. 388.
‡ *Ferrum*, 1913, vol. x. p. 257.
§ *Metallurgical and Chemical Engineering*, 1913, No. 8, vol. xi. p. 438.

IV.—*PHYSICAL PROPERTIES*.

Alkali Metals.—Some properties of the alkali metals have been determined by E. Rengade.* The following results are obtained :—

	Sodium.	Potassium.	Rubidium.	Cæsium.
Specific heat (solid) .	$0·2811 +$ $0·000233\ t$	$0·1728 +$ $0·000142\ t$	$0·0802 +$ $0·000153\ t$	$0·0522 +$ $0·000137\ t$
Specific heat (liquid)	$0·330$ at $98°$	$0·1422 +$ $0·000668\ t$	$0·0921 +$ $0·000026\ t$	$0·0604 +$ $0·000034\ t$
Heat of fusion . .	$27·21$	$14·67$	$6·144$	$3·766$
Atomic heat at $0°$.	$6·47$	$6·75$	$6·85$	$6·95$
Atomic heat of fusion ÷ absolute temperature of fusion . . .	$1·69$	$1·70$	$1·68$	$1·66$

Amorphous State in Metals.—In a paper read before Section B of the British Association Meeting of September 1913, W. Rosenhain † reviews the evidence in support of the theory of the existence of metals in the amorphous condition, and discusses the bearing of this theory in explaining the behaviour of metals when strained. That a metal may exist in the amorphous condition, as well as in the crystalline state, was suggested first by Beilby in 1904, and has received further support from the recent work of Bengough, Rosenhain, and others. The amorphous hypothesis is, however, opposed by Heyn and Tammann. The present paper discusses the probability of the existence of amorphous metal under three heads, as follows :

1. In considering the nature of the polished surfaces of metals, Beilby has recorded the microscopic evidence of flow and of the function of surface tension in producing the polished surface. Preliminary grinding of the flat surface is to be taken as a cutting action, whilst the final polish is obtained only by the production of a thin surface film of temporarily mobile metal which, under the influence of friction, flows over the whole surface, filling up the hollows of the scratches produced in the previous grinding processes, and yielding a highly polished surface of what is considered to be amorphous metal. The amorphous nature of this film is indicated by lightly etching the metal, when it is found that the old scratches will reappear in many places, the amorphous metal dissolving away more readily than the underlying crystalline material. It is now suggested that polishing involves actions of a chemical nature as well as those merely mechanical, and the difference in the properties of glass when polished with rouge from those of the same glass when polished with magnesia, is quoted in this connection. The effects of various powders employed in the polishing of silver are also contrasted, and the idea is put forward that the particles of the polishing powder

* *Comptes Rendus*, 1913, vol. clvi. p. 1897.
† *Engineering*, 1913, vol. xcvi. pp. 509-511, 537-539.

may be temporarily dissolved in the surface metal, and so assist in 'the breakdown of the crystalline structure which is taken to be fundamental in the polishing of metals.

On the analogy of the " polished " face presented by the free surfaces of all liquids, and of the essentially amorphous constitution of all liquids, it is argued that the production of a polished surface on a piece of metal involves the formation of an amorphous layer, so that it may be able to flow, when the polish acquired will result from the effects of surface tension.

It is pointed out that such a conception of the phenomenon of polishing implies the assumption by the altered surface material of the liquid, that is, the *amorphous*, condition, and that a polished surface is essentially of the nature of an undercooled liquid.

2. Having discussed the explanations offered by the amorphous theory of the polishing process, the author proceeds to consider how the amorphous hypothesis may be used in accounting for some of the facts observed when metal is plastically strained. It is to be supposed that when a metal is strained, thin layers of amorphous material are formed on every surface of internal slip occurring within the mass. Such an assumption is considered to be a logical conclusion from the previously described explanation of the process of polishing. The reappearance of slip bands in metal on polishing and etching, which is only obtained after severe strain, is explained by the higher solution pressure of the amorphous material (formed on the planes of slip) as compared with that of the crystalline metal. Slight strain is to be considered as producing only a comparatively small amount of amorphous metal on the slip planes, which would recrystallize rapidly before the polishing and etching could be effected.

A proposal to consider the slip band markings, which reappear on etching as twin lamellæ rather than amorphous metal, is rejected on the experimental evidence that, whereas twin crystals would tend to increase on annealing the strained metal, it has been found that the slip band markings will not reappear if the metal be annealed before polishing and etching. The improbability of twinning merely as the effect of work, apart from annealing, constitutes a further objection to the twin-crystal theory.

The incompatibility of the coexistence of crystalline and amorphous metal with the demands of the Phase Rule has been urged by some workers as an objection to the amorphous metal " method of explaining " deformation by slip, but it is pointed out that very little is yet known of the effect of pressure on the equilibria of metals, and that this is probably a most important variable when considering the conditions of stability in strained metal. Other considerations concerning the change in density involved in the crystalline-amorphous transformation are also discussed, more particularly in view of the fact that the straining of metals may involve either a positive or a negative pressure, and not merely the positive hydrostatic pressure usually encountered in consideration of equilibrium conditions.

In considering the properties of amorphous material, Beilby's assumption, that amorphous matter is usually hard as compared with its crystalline counterpart, is applied to the special case of the forcible retention of material in the condition of a solid solution by rapid cooling, and the resulting hardness is referred to as significant from the standpoint of the amorphous (undercooled liquid) theory.   This is, of course, only a special case, and, in metallurgy, merely concerns alloys ; but it goes to show that the metallic products may be hardened by forcing them to remain in the unstable condition of an undercooled liquid.   Results of work on non-metallic material indicate, however, that the generalization that undercooled liquids are hard, is capable of very wide application.

Turning again to the discussion of the hardening of metals by strain, it is argued that plasticity is essentially a property of crystalline metal, since the movement in a metal subjected to plastic strain takes place only along the gliding planes of the crystals.   An amorphous metal could not therefore accommodate itself to plastic strain—in other words, it would be characteristically hard and brittle.

In considering the hypothesis that the formation of amorphous metal enters into the mechanism of the yielding of metals under stress, the author first reviews other explanations of the phenomena.   Tammann has suggested that intercrystalline spaces exist between the polyhedral crystal grains of a metal ; the first effect of strain is supposed to be a filling up of these spaces, and, as the straining becomes more severe, a number of minute spaces appear in the interior of each crystal grain, due to the relative displacement of the crystalline lamellæ.   Whilst such a theory is in agreement with the experimental evidence as far as changes in the density of the metal are concerned, it can scarcely be reconciled with the fact that the intercrystalline boundaries in metals are surfaces of comparative strength.   Tammann's assumptions also meet with the further objection that a metal which was endowed with numerous small spaces in the interior of its crystal grains, would be weaker than the unstrained homogeneous metal, which is contrary to experimental evidence.

Admitting, then, the possibility of the formation of relatively hard amorphous metal on the planes of slip, in a metal undergoing plastic strain, it will be seen that this would account for a general hardening of the metal.   This supposition cannot, however, be used to explain the fact that the hardening of a strained metal is strictly limited as to sense. Thus, a piece of metal of which the elastic limit *in tension* has been raised by the application of a tensile force, has its elastic limit *in compression* lowered by the tensile strain.   It has also been shown that the hardening effect of cold work scarcely affects the resistance to alternating stresses.

These results may be explained by the conception of the existence of amorphous metal on the boundary surfaces of the crystal grains.   On this assumption, each crystal grain is surrounded by a very thin envelope of metal which, from its amorphous nature, is incapable of plastic strain ; it thus acts as an elastic membrane, and when the crystals are

deformed by tension, the amorphous envelope will tend to pull them back to their original shapes, thus lowering the elastic limit of the metal as a whole under compressive forces.

Dealing with the state of semi-plasticity which is a generally-recognized property of overstrained iron and steel, the author recalls the fact that, if a comparatively small load be applied to a bar of steel, immediately after the bar has been severely overstrained, the elongation produced by the small load is considerably greater than the elongation which such a load would have produced in the original metal. The metal will, however, recover in time from this abnormal plasticity, the recovery being more rapid the higher the temperature. In considering this phenomenon from the point of view of any crystalline theory of slip no adequate explanation has been obtained ; but, on the supposition that thin films of amorphous metal exist on the slip planes of the crystals of the metal, in conjunction with Beilby's conception of the temporary mobility possessed by such films, the author supposes a lubricating effect on the planes of slip, and, coupling this idea with that of the elastic forces exerted by the amorphous envelopes around the crystal grains, explains the mechanism of the semiplastic state in metals. The disappearance of this property with the lapse of time or on raising the temperature is determined by the recrystallization of the amorphous lubricant.

(3) Having discussed the various applications of the amorphous theory to the straining of metals, attention is turned to the third class of amorphous metal, and the theory is advanced that each one of the crystal grains of which a piece of metal is composed is cemented to its neighbours by a thin film of amorphous metal which covers its boundary faces. Unlike the amorphous metal produced by straining or polishing, however, this intercrystalline cement is to be regarded as constitutional, existing in both strained and annealed metal. The presence of this amorphous envelope is attributed either to the counterbalanced attractions of neighbouring crystal grains when the metal has not quite completely solidified from the liquid state, or, more probably, to a method of crystallization (on solidification) entailing the formation of "crystal units." This amorphous metal is truly undercooled liquid, and not of secondary origin as in the case of the amorphous metal produced by strain or polishing.

Evidence of the existence of this intercrystalline amorphous metal is given by the notable strength of the crystal boundaries shown by the fact that, in a pure metal, fracture normally takes its course through the crystal grains rather than round their boundaries.

The well-known fact that fineness of grain in a metal is conducive to strength also indicates the comparative rigidity of the crystal boundaries, whilst some recent observations on the nature of slip bands in iron point to the same conclusion.

Considerations of the supposed amorphous (or undercooled liquid) nature of the intercrystalline material led to the expectation that, with increase in temperature, the viscosity to which this material owes its strength would diminish more rapidly in proportion than would the strength of the crystalline grains, and this assumption has been verified by the results of

tensile tests on iron at high temperatures, in which it was found that, at
a certain temperature, the normal state of affairs was reversed, and, the
crystal boundaries becoming weak relative to the crystals themselves,
intercrystalline fracture took place, the crystal grains showing a marked
absence of deformation by slip.

Similar results have also been obtained with pure metals such as tin,
lead, gold, aluminium, and bismuth, and, although objections to the amor-
phous cement method of explaining these phenomena may be made on
the assumption that small amounts of impurities may form thin inter-
crystalline layers of fusible eutectics, it is considered that such objections
are no longer valid. These results are more fully discussed in this
Journal, pp. 119–139.

It is further argued that this intercrystalline metal, if present, should
show a higher vapour pressure than the bulk of the metal which is
crystalline, and experiments on the relative volatility of coarsely and
finely crystalline specimens of a number of metals when heated *in vacuo*,
are quoted in support of this contention.

With regard to the probability or otherwise of the formation of amor-
phous modifications of metals, the author points out that the amorphous
theory is capable of very wide application to the general behaviour of
metals, and until any other single theory is encountered which is equally
adequate in explaining the experimental evidence, it is suggested that
the amorphous theory be accepted as a working hypothesis.

**Anodic Behaviour of Alloys of Copper with Silver and
Mercury.**—In a paper on this subject D. Reichenstein * concludes that
negative depolarizers exist, the addition of which reduces the current
strength, and that the formation of alloys is a process occurring in both
kinds of polarization, oxygen and hydrogen being regarded as alloy-
forming elements.

Corrosion and Preservation of Metals.—Notes and observations
on corrosion and preservation of metals used in marine construction are
given by Lieutenant-Commander F. Lyon, U.S.N., † after an experience
of thirteen years' active service and three years' research. Corrosion, the
chemical decomposition of metal, is due to a difference in electric potential
between the metal and the liquid that wets the surface. Metals that are
absolutely dry do not corrode. The state of internal stress of material
depending on the mechanical work and heat treatment it has received
influences the manner and rate of its corrosion ; the more seriously
stressed material corrodes more rapidly. A bent plate or angle corrodes
more rapidly in and near the bend than the straight portion. Tubes
corrode more rapidly at the bends and flanges. Whereas copper alloy
castings seldom give trouble, they greatly increase the rate of corrosion
of less electro-positive material such as steel if in good metallic contact

* *Zeitschrift für Elektrochemie*, 1913, vol. xix. p. 520.
† *Engineer*, 1913, vol. cxvi. pp. 451–452.

with it. It is customary in such places to secure plates of zinc to the steel in order to protect it. The writer fails to see the value or necessity of this practice for the following reasons : (1) the zinc corrodes rapidly and becomes covered with a coating of zinc oxide, which is always found to be electro-negative to steel ; (2) in no case has he found steel connected to zinc corrode less in thirty days than when not so connected ; (3) a proper coat of paint between the alloy and steel surfaces will give efficient protection.

Galvanizing, electro-plating, and other such processes as means of protection to steel when continuously immersed are dangerous, and not to be recommended. It is deemed sufficient to provide the most homogeneous material possible, both chemically and physically, and to paint it in a proper manner. The painting of metal is discussed. With regard to boilers, condensers, &c., it has been definitely proved that any water showing 3 per cent. alkalinity with calcined sodium carbonate is noncorrosive to steel up to $422°$ F. If the alkalinity falls to $1·8-2·5$ per cent., bad pitting ensues. Much more harm is done by attempts to produce the correct amount of alkalinity in waters than by the small amount of acids which may ever enter an average boiler. The Cumberland method of preserving the interior surfaces of water-carrying pipes and circulating systems by raising the potential of the water to a value higher than at any point in the system appears to be the only practicable method, and gives excellent results when properly installed and attended.

Corrosion of Copper and Brass.—The corrosion of copper and brass tubes in sea water is the subject of a communication * describing trouble due to corrosion of copper condenser tubes on board ship. It is stated that the difficulty was finally met by employing solid-drawn copper tubes which had been carefully annealed before fitting ; and the conclusion is drawn that hard-worked material is peculiarly liable to corrosion. Other examples, taken from actual practice, are quoted in support of this suggestion.

Corrosion of Lead.—Experiments by A. Scala † indicate that the solubility of lead in distilled water is not appreciably affected by connecting the lead with zinc, tin, or copper to form a voltaic circuit. Experiments with alloys of lead and tin showed that the behaviour of the alloys could not be predicted by regarding them as made up of couples of tin and lead.

Corrosion of Lead by Lime.—The corrosion of lead by lime is attributed by W. Vaubel ‡ to the influence of calcium peroxide, which is formed wherever lime is exposed for long to air. Iron, when present, accelerates the action of the peroxide.

* *Engineering*, 1913, vol. xcv. p. 434.
†*Atti Reale Accademia dei Lincei*, 1913, vol. xxii. (i.) p. 155.
‡ *Zeitschrift für angewandte Chemie*, 1913, vol. xxvi. p. 423.

Corrosion of Lead by Water.—In a comparative study of the corrosive action of different waters on lead, H. Heap * reviews the previous work on the subject, and discusses the merits of different methods of testing. In his own experiments lengths of lead piping of about 10 yards were first used. With the pipes it is found that distilled water acts much more vigorously than lake water, whilst the presence of peaty matter diminishes the action. Owing to the difficulty of keeping the inner surface of the pipes in a constant condition, further experiments were made with pure lead foil, supported by glass rods attached to the stoppers closing the flasks. Air was completely excluded. Under these conditions pure distilled water has very little action. Oxygen accelerates the action ; whilst oxygen and carbon dioxide together cause rapid action, accompanied by the precipitation of " silky " lead carbonate. The action increases with the temperature up to 60°, and then falls off, until at 100° it is no more than at 5°. If exposed to the atmosphere, solution and precipitation of lead carbonate go on until no lead foil remains. Phosphates entirely prevent the attack, and the protective action of carbonates comes next to that of phosphates. Other salts have much less effect. Nitrates and some ammonium salts increase the corrosion, as do lime and aluminium sulphate. Hard waters containing carbonates are rendered less active by contact with peat, owing to removal of soluble salts.

Water from lead mines in limestone districts is commonly free from lead, owing to precipitation of the carbonate.

Density of Aluminium.—In a previous paper † F. J. Brislee gave the results of a series of determinations on the density of aluminium, and the extremely slight change of density with work was referred to as remarkable. The investigation has been continued with a view to throwing further light on the influence of work on the metal, and a large number of results are given.‡

Cast Metal.—The metal used for this series was cut from the *middle* of an 80 lb. bar about 4 inches square.

Composition. Per Cent.			Treatment.	Density.
Si 0·33	.	.	As cast	$2 \cdot 7059 \pm 0 \cdot 00044$ (mean of 9)
Fe 0·56	.	.	Annealed 14 hours at 450° C.	$2 \cdot 7060 \pm 0 \cdot 0002$ (mean of 9)
Cu trace	.	.	Annealed 28 hours at 450° C.	$2 \cdot 7067 \pm 0 \cdot 0002$ (mean of 9)
Al 99·11	.	.	Annealed 42 hours at 450° C.	$2 \cdot 7060 \pm 0 \cdot 0002$ (mean of 9)

In all cases the values given for density are corrected for buoyancy and referred to water at 4° C.

These determinations were repeated on a purer sample of metal (Si 0·21, Fe 0·15, Cu trace, Al 99·64) ; specimens were, however, cut from the *top* of the ingot.

* *Journal of the Society of Chemical Industry*, 1913, vol. xxxii. pp. 771, 811, 847.
† See abstract, *Journal of the Institute of Metals*, No. 2, 1912, vol. viii. p. 316.
‡ *Transactions of the Faraday Society*, 1913, vol. ix. (1 and 2), pp. 162–173.

Treatment. Density.
As cast . . . . . 2·7031 ± 0·0006 (mean of 12)
Annealed in 48 hours . . . 2·7029 ± 0·0004 (,, 10)

In order to ascertain whether a difference existed between top and bottom of an ingot, specimens were cut from as near the two ends of a couple of ingots as possible.

Treatment.	Density.
As cast . . .	Ingot No. 1—top 2·6952 ± 0·0009 (mean of 9) bottom 2·6992 ± 0·0005 (mean of 9)
	Ingot No. 2—top 2·6933 ± 0·0032 (mean of 9) bottom 2·7040 ± 0·0012 (mean of 9)

The effect of work on the density was now investigated by determinations before and after annealing on hard-rolled and drawn material.

Hard-rolled and Drawn Metal.—Cast slab rolled down from 2 inch to 0·018 inch without annealing.

Treatment. Density.
As rolled . . . . . 2·7089 ± 0·0008 (mean of 23)
Annealed at 450° C. 14 hours . 2·7098 ± 00003 (mean of 23)

Other forms of worked material were tested as follows :—

Material.	Density.	
	Hard-drawn.	Annealed.
Wire, drawn from 0·3 in. to 0·072 in. diam. without annealing	2·7026 ± 0·0004 (mean of 15)	2·7057 ± 0·0005 (mean of 10)
⅝ inch round bar, hard-drawn	2·7056 ± 0·00024 (mean of 10)	2·7079 ± 0·00020 (mean of 10)
0·800 × 0·435 inch rectangular bar	2·7112 ± 0·0003 (mean of 11)	2·7127 ± 0·0004 (mean of 10)

In the above three cases the work done upon the metal was apparently greatest in the case of the 0·072 inch wire, and next on the ⅝th inch rod, being least in the case of the rectangular bar ; but the densities are in the *reverse* order, and all increase on annealing. Other results make it evident that the density of aluminium *does not necessarily increase with the amount of work put on it.* A further sample of wire drawn to 0·064 inch diameter gave a density (mean of 10) of 2·7022, and after annealing of 2·7051. The difference is about ten times the error of measurement. The following results were obtained on some cold-rolled sheet 0·080 inch thick (Si 0·29, Fe 0·38, Cu trace, Al 99·33).

Treatment. Density.
As rolled . . . . . 2·7076 ± 0·0002
Annealed 2 hours at 560° C. . . 2·7086 ± 0·0002
Annealed 22 hours at 560° C. . . 2·7085 ± 0·0001

Structure of Aluminium.—A dilute solution of hydrofluoric acid (1 to 8), with subsequent immersion in nitric acid (60 per cent.) for a few seconds, is recommended for etching the polished surface of the metal.

Polished and etched surfaces of aluminium in the cold-worked state examined under the microscope are devoid of crystalline structure, the only feature being flow lines in the direction of work. The hard-drawn specimens with a density greater than 2·7030 showed traces of a crystalline structure. Increase in density was always accompanied by a change in structure towards the crystalline state.

The change from the structureless or amorphous state of severely cold-worked metal to the crystalline appears to take place very slowly, and cold-worked metal having an elongation of 3 to 4 per cent. can be annealed so as to have an elongation of 30 per cent. and yet show only a very slight change in structure. It is evident that the density of aluminium varies very considerably, and that under suitable conditions the density of the cast metal may exceed that of the worked. It is difficult to see how the lower density of worked metal is to be accounted for on grounds other than a change from the crystalline to the amorphous state.

The paper is illustrated with several microphotographs of cast, cold-worked, and annealed aluminium.

Elastic Modulus of Aluminium.—The elastic modulus of aluminium has been redetermined by F. J. Brislee.* Metal of a high degree of purity was used. Chemical analysis gave the following results :—

		Per Cent.
Silicon	. . . .	0·35
Iron .	. . . .	0·28
Copper	. . . .	trace
Aluminium	. . . .	99·37
		100·00

The modulus was determined by two distinct methods—(1) by the bending of rods supported at each end on knife edges and loaded in the middle ; (2) by the stretching of wires loaded at one end and fixed at the other.

Both the bend and the stretch were measured with screw micrometers, contact being electrically recorded. In the case of the bending experiments, square, round, rectangular, and semicircular bars were employed. Results repeated to within 1–2 per cent. with frequent exact agreements. General mean of results by bending :—

Elastic Modulus = 6918 kilogrammes per square millimetre (4393 tons per square inch).

In taking this mean certain abnormal results were excluded, viz. those on the semicircular bars which gave a mean result $E = 7217$ kilogrammes per square millimetre, and the results obtained along the long axis of the rectangular bars, which gave a mean value $E = 6574$ kilogrammes per square millimetre. In the case of the semicircular bars low tensile strength and the nature of the fracture and micro-

* *Transactions of the Faraday Society*, 1913, Nos. 1 and 2, vol. ix. pp. 155–161.

structure pointed to the material having been overworked. The density of $\frac{3}{8}$th inch round and square bars and the semicircular bars showed a variation with the elasticity :—

Bar.						Density.	Mean Elasticity.
Square	.	.	.	.	.	$2 \cdot 7039 \pm 0 \cdot 0001$	6841
Round	.	.	.	.	.	$2 \cdot 7052 \pm 0 \cdot 0001$	6973
Semicircular	.	.	.	.	.	$2 \cdot 7095 \pm 0 \cdot 0001$	7217

In the case of the stretching of wires, measurements repeated on the same wire to 2 per cent. Measurements made in rapid succession gave increasingly higher results due to fatigue, and it was necessary to allow long intervals of rest. General mean of results on wire :—

Elastic Modulus=6892 kilogrammes per square millimetre (4376 tons per square inch).

Overworked material gives a considerably higher modulus. One sample of wire over-drawn to such an extent that it was impossible to bend it at right angles without fracture gave a result $E = 7323$ kilogrammes per square millimetre. General mean of both series :—

Elastic Modulus=6905 kilogrammes per square millimetre (4384 tons per square inch).

The results are somewhat lower than those of Slötte, Katzenelsohn, and Meyer recorded in Landolt and Bornstein's tables. The presence of an increased amount of iron, silicon, or copper would cause a considerable rise in the modulus. The higher values obtained above are probably due to overwork and fatigue, and do not represent a desirable condition for the technical metal. The passage of the metal into the amorphous state under the influence of work has been pointed out in a previous paper, and that in the amorphous state the metal should possess a higher elastic modulus is to be expected.

Further results bearing on the change from the crystalline to the amorphous state are promised.

Effect of Annealing on the Structure of Alloys.—A. Portevin *
reviews at length the effect of annealing on the structure of alloys, and summarizes the results of his own work, and those of other investigators as follows :

(A) The changes brought about by annealing within a field of the equilibrium diagram are due to the following influences—

    1. The return to a state of mechanical equilibrium with the removal of internal stresses.

    2. The return to a state of physico-chemical equilibrium resulting in the disappearance of phases which are not in equilibrium, while solid solutions become chemically homogeneous.

* *Revue de Métallurgie*, 1913, vol. x. pp. 677–721.

3. The recovery of structural equilibrium leading to the appearance under the microscope of phases in equilibrium, the coalescence of structural elements and the accentuation of the chemical heterogeneity in a two-phase field.

4. The recovery of crystalline equilibrium accompanied by enlargement of grain size and general or local recrystallization.

(*B*) When lines of transformation in the diagram are crossed, annealing may then produce—

1. A physico-chemically or structurally unstable condition. These are quenching effects.

2. Changes in arrangement of stable constituents, depending on the crystalline structure and chemical heterogeneity of the intermediate phases stable above the lines crossed. These phases exercise a directional effect causing a kind of hereditary structure.

3. Crystalline modifications resulting from polymorphic transformations of phases.

The tendency to return to a state of equilibrium becomes greater as the temperature rises. The final effect of annealing is thus a function of the temperature and of the time of annealing. The results of annealing are also influenced by the character of the alloy itself, such as the amount of work it has received, the method of deformation of the crystalline elements, the presence of impurities, &c.

Electrolytic Methods for Preventing Corrosion.—An abstract of a lecture delivered before a joint-meeting of the Faraday Society and the Society of Chemical Industry, by W. W. Haldane Gee * deals with electrolytic methods for preventing corrosion.

Corrosion of metals may be lessened or prevented in two ways—

(1) By connecting the metal to be protected to a more electro-positive metal, so as to produce a primary cell.

(2) By making the metal to be protected the cathode in an electrolytic cell supplied by external electrical pressure.

1. *Primary Cell Method.*—The chief methods of connection and arrangements of parts are indicated. Of special importance is effective voltage. The greater the current strength, the greater the protective value of the cathode from corrosion. When hydrogen is formed at the cathode, the pressure or *over-voltage* necessary to liberate the gas may be important. Thus zinc is a good protector for brass, the over-voltage being small, and the current large ; it is a poor protector for tin, the over-voltage of tin being especially high. The prevention of corrosion of a metal by direct application to it of a more electro-positive metal was suggested by Sir H. Davy. His experiments on the protection from corrosion of the copper sheathing of ships, detailed in the *Transactions of the Royal Society*, showed that a relatively small area of iron or zinc would protect copper ; the method had to be abandoned owing to the clean copper forming a surface on which shellfish and seaweed flourished, making the bottoms very foul. Diegel, in 1898, confirmed Davy's results that both zinc and iron would

* *Transactions of the Faraday Society*, 1913, No. 1 and 2, vol. ix. pp. 115–124.

act as protectors of copper and brass. E. Cohen, in 1902, showed that the method might be used with advantage by marine engineers for the protection of condenser tubes, &c.

More recently, Engineer Rear-Admiral Corner has detailed cases where the presence of iron strongly counteracts the corrosion of copper and brass. Iron is more efficient than zinc, owing to the possibility of maintaining a better metallic contact.

Protectors made of aluminium and aluminium alloys are used in some systems. Although aluminium is a very electro-positive metal, some precautions must be taken in its use. Thus, in sodium chloride solution, it is electro-negative to zinc, and the latter metal corrodes. At 70° C. the potential difference changes and aluminium dissolves ; on cooling, the reverse change takes place.

The use of zinc for the protection of steam-boilers has been in practice for about eighty years. There are results of experience which show that if used in sufficient, quantity, and properly applied and connected, the protection afforded is *perfect*. It is advised to use 1 square foot of zinc to 50 to 100 square feet boiler surface. H.M.S. *Crocodile* is said to have used 425 to 630 lb. rolled zinc per boiler per annum. A case is mentioned where slabs of zinc $12 \times 12 \times 1\frac{1}{2}$ inches disappeared in six weeks.

2. *Use of External Electrical Pressure.*—Now that the supply of cheap electrical energy is so general, the use of an external pressure for protection against corrosion deserves careful attention.

Experiments made at the Manchester School of Technology show that quite a low value of current density is sufficient for adequate protection. This current may be calculated from the loss due to corrosion, in accordance with Faraday's law. In a case in which the loss of iron in sea water was equivalent to about 0·004 ampere per square foot, the application of this current density gave protection. In another case, in which $\frac{1}{5}$th to $\frac{1}{1000}$th normal sulphuric acid was used, current densities of 0·144 to 0·072 ampere per square foot proved sufficient. The Cumberland process of electrolytic protection is described, and its manner of application indicated. Anodes of carbon or iron are used, and continuity of electrical supply by both dynamo and storage cells. Rheostats and ammeter are provided, so that the current density may be controlled. The results of the application of this system to many marine and land boilers have been satisfactory. The patents of Harris and Anderson are devoted mainly to the protection of surface condenser tubes. They have shown that a minimum current density of 0·0012 ampere per square foot is sufficient for protection. In the case of a certain condenser of 1025 square feet area, 2 amperes at 2 volts is continuously supplied. This represents an annual expenditure of energy equal to 35 Board of Trade units. Other applications of the method are described.

Commercial success demands that—

(*a*) The current density should be sufficient, and equally distributed by a sufficient number of anodes.

(*b*) Anodes and electrical connections should be well insulated.

(c) The nature of the anodes should be rightly selected. In some cases they may be soluble, in others they must be insoluble.

Electrical Conductivity of Copper-Zinc Alloys.—These alloys have again been examined by N. Pushin and W. Rjaschsky,* using cast rods annealed for 48 to 120 hours. No account is taken of Carpenter's work on the β-phase, and this constituent is assumed to be homogeneous. The resistance curve has three maxima, of which the first corresponds with the formation of the α-solid solutions, and the others with the compounds Cu_2Zn_3 and $CuZn_6$ respectively. (The authors do not accept the former of these compounds, but regard the maximum merely as indicating the limit of saturation of the γ-solid solution.) The curve of the temperature-coefficients has three distinct maxima, corresponding with the compounds $CuZn$, $CuZn_2$, and $CuZn_6$ respectively. From 90 to 100 atomic per cent. of zinc the resistance is nearly constant, whilst the temperature coefficient increases.

The authors conclude that the definite compounds of copper and zinc are $CuZn$, $CuZn_2$, and $CuZn_6$, and that the supposed compounds Cu_2Zn and Cu_2Zn_3 do not exist. They point out that $CuZn_6$ has several analogues, such as $NaCd_6$ and $CsHg_6$. A compound, $CuZn_{10}$, corresponding with $CsHg_{10}$, is possibly indicated in the curves.

Electrical Properties of the Alkali Metals and of Rhodium and Iridium.—L. Hackspill and W. Broniewski † have determined the principal electrical properties of these metals, the alkali metals being first thoroughly purified by distillation. The purified metal is then introduced into exhausted capillary tubes. By using a recording galvanometric arrangement, it is found that the curve of thermo-electromotive force of rubidium shows an abrupt change of direction at the melting point, whilst that of cæsium actually reverses its direction. There is a difference of potential of 20 microvolts between solid and liquid cæsium. The electromotive force of solution of the four alkali metals, determined in aluminium-chloride solution, differs very little. The electromotive force of potassium and rubidium is hardly changed by amalgamation, whilst that of sodium and cæsium is considerably diminished, probably owing to chemical combination.

Resistance and thermo-electrical measurements indicate that rhodium undergoes a transformation at a temperature near that of liquid air, but that iridium is not affected.

Errors in a Copper Voltameter.—The discrepancies between the results obtained with a copper and a silver voltameter have been studied by N. Dhar,‡ who is, however, unable to explain the discrepancies, and concludes that the copper voltameter gives inaccurate results for some

* *Zeitschrift für anorganische Chemie*, 1913, vol. lxxxii. p. 50.
† *Annales de Chimie et de Physique*, 1913, Ser. 8, vol. xxix. p. 455.
‡ *Zeitschrift für Elektrochemie*, 1913, vol. xix. p. 746.

reason not fully understood, in spite of numerous investigations dealing with the subject.

Graphical Representation of Three Variables.—A method of graphical representation is described by M. von Pirani,* suitable for cases in which three variables, such as concentration, temperature, and electrical resistance are concerned. The ordinary method of a three-dimensional diagram, represented in perspective, gives the clearest general view, but does not lend itself to numerical interpolation. The method of plotting only two variables on each curve, and so obtaining a family of curves, each corresponding with a definite value of the third variable, does not give a general picture. The new method cannot well be described without diagrams, but depends on the erection of ordinates, each of which bears a double scale, one scale being constant throughout, whilst the other moves up or down as required.

Hall Effect.—It is found by A. W. Smith † that the Hall and Nernst effects in Monel metal and Nichrome are affected by temperature in the same way as in nickel, cobalt, and iron. A transverse magnetic field affects the resistance of these alloys in the same way as that of nickel, but to a less extent. Occluded hydrogen, even in large quantity, is without influence on the Hall effect in palladium.

Heat Capacity of Metals.—The heat capacity of a number of metals has been very accurately determined by E. H. Griffiths and E. Griffiths,‡ using very large masses of metal (1–4 kilogrammes) heating electrically, and determining temperatures by means of platinum resistance thermometers. The metals are cast and turned to cylindrical form, so as to fit a thin copper case, in order to provide the same radiating surface in every experiment. Silver, copper, cadmium, lead, tin, and zinc have been examined between $0°$ and $100°$, and a parabolic relation is found to exist between heat capacity and temperature within this range. Nernst's values are in good agreement with those of the authors', and it is proposed to continue the experiments down to very low temperatures, at which the parabolic formula is unlikely to hold good.

Heat of Solution.—New determinations have been made by E. E. Somermeier,§ using a vacuum flask calorimeter. Zinc, aluminium, and magnesium were dissolved in dilute hydrochloric acid. The results are in fair agreement with those of previous observers, and contain nothing new.

Magnetism of Antimony Alloys.—According to P. Leroux, ‖ the magnetic properties of alloys of tin and antimony have a well-marked

* *Internationale Zeitschrift für Metallographie*, 1913, vol. iv. p. 263.
† *Physical Review*, 1913, Ser. 2, vol. ii. p. 339.
‡ *Philosophical Transactions*, 1913, vol. ccxiii-A. p. 119.
§ *Physical Review*, 1913, Ser. 2, vol. ii. p. 141.
‖ *Comptes Rendus*, 1913, vol. clvi. p. 1764.

maximum at 95 per cent. of antimony, which is not readily explicable. A break in the curve indicates the compound SbSn. The lead-antimony curve has a pronounced minimum at 85 per cent. of antimony. A similar break was found by N. Pushin in the electromotive force curve of these alloys. A compound is suggested, but no formula is given.

Magnetism of Manganese, Copper-Manganese, and Chromium.—Experiments by K. Ihde [*] show that manganese, even when free from iron, has ferromagnetic properties, with a maximum in the susceptibility curve for weak fields. Heating massive manganese to 600° and quenching in water alters its magnetic properties. Manganese in a powdered condition has a greater magnetic moment than the massive metal, and the moment increases with diminishing size of grain. Copper-manganese alloys with 30 per cent. of manganese have a much higher susceptibility than manganese.

Chromium is also more strongly magnetic in the state of powder than in the massive form.

Melting Points of Refractory Metals.—Using the micropyrometer, in which minute particles are heated electrically on a strip of platinum or iridium, G. K. Burgess and R. G. Waltenberg [†] find the following probable melting points of certain pure metals, slight extrapolation having been necessary in a few cases :—

						Degrees Cent.
Nickel	.	.	.	.	.	1452 ± 3
Cobalt	.	.	.	.	.	1478 ± 5
Iron	.	.	.	.	.	1530 ± 5
Manganese	.	.	.	.	.	1260 ± 20
Chromium	.	.	.	.	.	$1520 ?$
Vanadium	.	.	.	.	.	1720 ± 30
Titanium	.	.	.	.	.	1795 ± 15

Modulus of Elasticity, and its Relation to other Physical Quantities.—A. H. Stuart [‡] finds that the modulus of elasticity is a linear function of H where

$$H = \frac{\text{Density} \times \text{Specific Heat}}{\text{Coefficient of Linear Expansion}}.$$

If one gramme of metal is taken in the form of a rod, then $H =$ number of calories of heat which would be absorbed by the rod in doubling its length under the action of the heat alone. The following Table is given :—

* *Annalen der Physik*, 1913, Ser. 4, vol. xli. p. 829.
† *Zeitschrift für anorganische Chemie*, 1913, vol. lxxxii. p. 361 ; also in *Journal of Washington Academy of Sciences*, 1913, vol. iii p. 371.
‡ *Proceedings of the Institution of Mechanical Engineers*, 1912, pp. 1155-1159.

Metal.	Density, Grammes per Cubic Centimetre.	Specific Heat.	Coefficient of Linear Expansion.	H. (in calories).	E. Kilogrammes per Sq. Milli-metre.
Aluminium .	2·58	0·2270	$2·313 \times 10^5$	$2·54 \times 10^4$	$6·71 \times 10^3$
Copper . .	8·9	0·0920	1·666 ,,	4·91 ,,	10·98 ,,
Gold . .	19·3	0·0316	1·443 ,,	4·23 ,,	9·68 ,,
Iron . .	7·86	0·1130	1·140 ,,	7·80 ,,	18·46 ,,
Lead . .	11·34	0·0299	2·955 ,,	1·15 ,,	1·8 ,,
Platinum .	21·48	0·0323	0·899 ,,	7·72 ,,	17·04 ,,
Silver . .	10·5	0·0568	1·921 ,,	3·09 ,,	6·87 ,,
Tin . .	7·3	0·0559	2·234 ,,	1·83 ,,	4·17 ,,
Zinc . .	7·14	0·096	2·905 ,,	2·36 ,,	8·64 ,,
Brass . .	8·7	0·092	1·859 ,,	4·30 ,,	9·65 ,,

Plotting H against the modulus of elasticity, the points are found to lie about a straight line whose equation determined from the graph is $E = 0·225$ H.

Calculating the modulus from this equation the following results are obtained :—

Metal.	H.	E. Kilogrammes per Sq. Millimetres. (Observed.)	$E = 0·225$ H. Kilogrammes per Sq. Millimetre. (Calculated.)
Aluminium	$2·54 \times 10^4$	$6·71 \times 10^3$	$5·73 \times 10^3$
Copper	4·91 ,,	10·98 ,,	11·00 ,,
Gold	4·23 ,,	9·68 ,,	9·55 ,,
Iron	7·80 ,,	18·46 ,,	17·60 ,,
Lead	1·15 ,,	1·8 ,,	2·59 ,,
Platinum	7·72 ,,	17·04 ,,	17·30 ,,
Silver	3·09 ,,	6·87 ,,	6·96 ,,
Tin	1·83 ,,	4·17 ,,	4·13 ,,
Zinc	2·36 ,,	8·64 ,,	5·32 ,,
Brass	4·30 ,,	9·65 ,,	9·68 ,,

Zinc, aluminium, lead, and iron are somewhat out of alignment on the curve, zinc being the greatest offender. These variations may be accounted for by the fact that the modulus of elasticity of all metals is influenced by temperature condition as regards mechanical work and heat treatment, and presence of impurities. Zinc shows these variations to an almost unequalled extent. The modulus of zinc has been shown by von Miller to vary as much as 20 per cent. according to its condition, whilst there is a falling off of 33 per cent. from $0°-100°$ C. Latzenelsohn has shown that the modulus of elasticity of aluminium falls 19·5 per cent. from $0°-100°$ C. Lead has a very low modulus. In the case of iron small quantities of impurities cause large variations in the modulus.

Optical Constants of Sodium and Potassium.—It has been found possible by R. W. Duncan and R. C. Duncan * to obtain and preserve indefinitely bright surfaces of sodium and potassium by melting the metal under oil, and introducing it while molten into an evacuated vessel with glass windows, so that the metal solidifies in contact with the glass. Metallic sodium has the lowest index of refraction and the highest reflecting power of any known metal. Its refractive index has a minimum near the sodium line. Potassium has a very low refractive index, but its reflecting power is less than that of sodium or silver.

Palladium in Hydrogen.—Heating and cooling curves of palladium in hydrogen have been determined by J. H. Andrew and A. Holt. † The metal *in vacuo* shows slight discontinuities in the inverse-rate curves in the neighbourhood of $150° - 200°$. Palladium black always retains its activity towards hydrogen, whilst the compact metal loses its power of occluding hydrogen, and this is only restored, and then only temporarily, by heating in air. The original black is amorphous, and heating the compact metal probably forms a layer of oxide, which is then reduced by the hydrogen. The amorphous layer thus formed slowly crystallizes.

The heating curves of palladium in hydrogen show an absorption of heat beginning at about $95°$, and a rapid development of heat at $135°$. The process is reversible, but the temperature, for foil and compact metal, varies with the time the metal has remained in contact with the gas in the cold. Palladium black is not affected in this way. From $150°$ upwards, the quantity of gas retained does not vary greatly until the melting point is reached.

The results are explained by the rapid occlusion of hydrogen by the amorphous metal, which serves as a medium for the transfer of gas to the crystalline metal. It appears that the gas is absorbed in the molecular condition, and then dissociates, the thermal effects being mainly accounted for by dissociation and recombination.

Physical Constants as Periodic Functions of the Atomic Weight.—It is shown by W. Biltz ‡ that the boiling points of the elements, like their melting points, are a periodic function of the atomic weight. A few of the metals show irregularities, due apparently to molecular association. The electrical conductivity of the metals is also a periodic property, as is the absorptive power for light. The curve of the refractive index is almost exactly the inverse of that of electrical conductivity. The hardness is also a periodic function of the atomic weight.

Polymorphism of Zinc. — Calorimetric observations by P. N. Laschtschenko § fix the temperature of the polymorphic transformation

* *Physical Review*, 1913, Ser. 2, vol. ii. p. 294.
† *Proceedings of the Royal Society*, 1913, vol. lxxxix.-A, p. 170.
‡ *Zeitschrift für Elektrochemie*, 1913, vol. xix. p. 613.
§ *Journal of the Russian Physico-Chemical Society*, 1913, vol. xlv. p. 552.

of zinc at 340°–350° and the heat of transformation at 0·19 calories'per gramme-atom. The heat of fusion is 1·73 calories per gramme-atom.

Resilience of Copper and its Alloys.—Shock tests of copper and its alloys at different temperatures have been carried out by L. Guillet and V. Bernard,* rolled and annealed bars being used. Except copper-nickel, all the specimens show a maximum of fragility at 300°–400°. There is often a maximum resilience near 100°. Fragility tests do not indicate the best rolling temperatures.

Solid Solutions.—In a long and comprehensive memoir, A. Bruni † sums up his work on the nature of solid solutions. This includes much work on diffusion in solid metals. Further evidence of this taking place at moderate temperatures has been obtained by forming a wire with 540 alternate layers of copper and nickel, the total thickness being 0·25 millimetres. Heating merely to 100° for six hours produced a distinct increase of the electrical resistance, which became considerably greater after twenty-seven hours. A comparatively short heating at 550° produced a homogeneous solid solution. The dimensions of the original layers were comparable with those of a colloidal solution.

Specific Heat of Cold-Worked Metals. — According to C. Chappell and M. Levin,‡ the differences in specific heat between cold-worked alloys (steels and tin-bronzes) and the same alloys after annealing in a vacuum fall within the limits of experimental error, although on the whole the cold-worked specimens give a slightly higher value. The density of the cold-worked specimens is always less than in the annealed state, the difference being on an average 0·3 per cent.

Strength, Ductility, Density, and Hardness of Cast Aluminium and Bronze. — The relation between mechanical and physical properties has been examined for several cast metals by W. Wyss.§ The bars used were 110 centimetres long and 3 centimetres square, and were tested on a 10-ton recording bending machine. The material described as commercial cast aluminium was really an alloy containing 8 per cent. of zinc and 1·5 per cent. of copper. As the yield of this metal was greater than that provided for in the machine, the bars were cut in half and tested separately. It was found that the half which was uppermost during casting (in an inclined position) was always the stronger, the ratio obtained from eight bars being 100 : 81. Similar results were obtained with two bars of pure aluminium, the ratio being 100 : 78, the differences in the angle of bending being still greater. Experiments with bars cast in different positions showed that the strongest part was always that farthest removed from the gate, and by further modifying the conditions of casting it was found that the

* *Comptes Rendus*, 1913, vol. clvi. p. 1899.
† *Memoria della Reale Accademia dei Lincei*, 1912, p. 1.
‡ *Ferrum*, 1913, vol. x. p. 271.
§ *Ibid.*, pp. 167–207.

increased strength and toughness were due to chilling, slowly cooled bars being regularly weaker. The density follows the strength fairly closely. The hardness is fairly uniform, except that the strong, rapidly cooled end of the bar has an increased hardness.

With tin-bronze there is an optimum rate of cooling, bars cooled either more or less rapidly being weaker. Micrographic examination confirms the results. Cast iron is much less influenced by the above conditions than either aluminium or bronze.

Testing of Bearing Metals.—Mechanical tests peculiarly adapted to the testing of bearing metals are described * by T. D. Lynch.

The original " babbit metal " for lining bearings is a " tin-base " alloy containing about 90 per cent. tin, the remainder being copper and antimony.

On account of the high price of tin and the increasing consumption of bearing-metal alloys, attempts to replace the original babbit metal by a cheaper alloy have been general, and as a result there is a growing tendency for " lead-base " alloys to replace the more expensive " tin-base " bearing metals which comprise the original " babbit metal," and other mixtures. It is stated, however, that bearing-metal alloys containing lead require much more careful consideration as to composition and pouring temperature than alloys rich in tin, and tests are described and results given in the present paper indicating the most suitable heat treatment for the " lead-base " alloys.

Friction tests, in which the bearing alloy under investigation carried a motor shaft on to which was keyed an eccentric weight of 265 lb., proved abortive, the motor going to pieces whilst the bearing remained in good condition. Another still more strenuous test on the same lines failed to produce appreciable wear in the bearing.

It is concluded that tests of the bearing in actual service furnish the only reliable data as to the qualities of the lining alloy.

Measurements of comparative values can be obtained, however, by mechanical tests pure and simple, which may be made on samples of the metal from the mixing pot. By such means it is possible to insure that all melts of bearing metal should be up to a specified standard.

The properties tested were hardness, by the Brinell test, and malleability, by a drop-hammer apparatus specially designed for the purpose.

A series of tests is described which were conducted on twelve samples of a " lead-base " bearing-metal alloy which had been melted and cast at different temperatures. The results are given in a number of curves and photographs which show the very marked effect of melting and casting temperature on the malleability of the alloy. As a result of these and other tests it is concluded that whilst $460°$ C. is the best casting temperature for both " lead-base " and " tin-base " bearing alloys, a more accurate temperature regulation is necessary in the case of " lead-base " material than for " tin-base " alloy if equally good results are to be obtained in both cases.

* *Metal Industry*, 1913, vol. v. p. 317.

A Brinell hardness number of 23·5 is stated to be satisfactory for "lead-base" alloy, the corresponding figure for "tin-base" alloy being 30. The shell to be babbited should be previously warmed to 100°–150° C. before casting the alloy, and must not be jarred in any way whilst the babbit metal is solidifying, or the lining will be brittle. The primary importance of employing pure metals for making the alloys is emphasized in all cases.

Thermal and Electrical Conductivities of Alkali Metals.— Measurements by J. W. Hornbeck [*] show that the temperature coefficient of the resistance of sodium and potassium is extremely high. The thermal conductivity falls slightly with increasing temperature, whilst that of the liquid alloy of sodium and potassium rises slightly. The ratio of the thermal to the electrical conductivity for the alkali metals is exceptionally high. A modification of the electron theory of metallic conduction is proposed.

Thermal and Electrical Properties of Antimony-Bismuth Alloys.—G. Gehlhoff and F. Neumeier [†] have examined the alloys of bismuth and antimony over a range of temperature from $-190°$ to $+100°$, the properties determined being the thermal and electrical conductivity and the thermo-electric power. The thermal conductivity passes for alloys rich in bismuth through a minimum at about $-90°$. In the series of alloys the thermal and electrical conductivities are a minimum for the alloys with 10 per cent. of antimony. The temperature-coefficient of the conductivity has both a minimum and a maximum in this neighbourhood.

Thermal Treatment of Metals and Alloys.—The principal results on this subject, so far as the non-ferrous metals are concerned, are summarized by W. Müller.[‡] The metals and alloys treated are : Copper, zinc, nickel, aluminium, brass, bronze $(91:9$ and $90:6:4)$, aluminium-bronze, cupro-nickel, and magnalium. All the data have been previously published.

Transport of Mercury through Tinned Copper Wires.—The action of tinned copper wires as a siphon in conveying mercury has been studied by Jaubert de Beaujeu.[§] Observations exist as far back as 1830. It is found that the flow is independent (within limits) of the hydrostatic pressure of the mercury, and is due entirely to capillary forces, as in the well known siphoning of water by a strip of cloth.

Vapour Pressure of Metals.—Very exact determinations have been made by H. von Wartenberg,[||] using the dynamic method, in which

* *Physical Review*, 1913, No. 2, vol. ii.
† *Berichte der deutschen physikalischen Gesellschaft*, 1913, vol. xv. p. 876.
‡ *Metall und Erz*, 1913, vol. x. p. 219.
§ *Journal de Physique*, 1913, Ser. 5, vol. iii. p. 706.
|| *Zeitschrift für Elektrochemie*, 1913, vol. xix. p. 482.

the metal is heated in a boat in a porcelain tube in a current of hydrogen. The vapour pressure is calculated from the ratio of metal to hydrogen in the vapour. In the following table p represents the vapour pressure in atmospheres, whilst λ is the heat of vaporization calculated from the curves :

Metal.					Temperature, Degrees C.	p	λ.
Lead	.	.	.	.	808 996 1178	$1 \cdot 05 \times 10^{-4}$ $2 \cdot 30 \times 10^{-3}$ $2 \cdot 20 \times 10^{-2}$	44,000
Silver	.	.	.	.	1178 1316 1435	$1 \cdot 90 \times 10^{-4}$ $1 \cdot 08 \times 10^{-3}$ $5 \cdot 10 \times 10^{-3}$	60,800
Thallium	.	.	.	.	634 783 907	$7 \cdot 40 \times 10^{-5}$ $1 \cdot 75 \times 10^{-3}$ $3 \cdot 20 \times 10^{-2}$	38,200

Extrapolation gives the boiling points—Lead, $1630 \pm 20°$, Silver $2100°$, Thallium $1306°$. Copper and platinum at $1360°$ have a vapour pressure less than 10^{-5} atmospheres.

Volatilization of Metals.—The volatilization of metals at temperatures much below their boiling point has been further studied by G. W. C. Kaye and D. Ewen.* In addition to ordinary evaporation, particles are shot off in a rectilinear direction, so that images of an aperture or obstacle may be obtained. In the case of iron, the range of such particles is only a centimetre or so. The surface of the emitting strip shows regularly oriented pitting. Direct current heating produces much more effect than external heating. It is suggested that the particles thus expelled carry an electric charge, but the difference between these and the particles involved in ordinary evaporation may be only one of size.

Volatilization of Zinc and Cadmium.—Further experiments by T. K. Nair and T. Turner † have been directed to determining the influence of pressure. The temperature at which volatilization becomes appreciable is raised by pressure, the first small increments of pressure starting from a good vacuum having the greatest effect. The volatility-temperature curve for any given pressure is practically linear for the greater part of its length, whilst the pressure-temperature curve for equal rates of volatilization rises steeply at first, becoming linear beyond about 80 millimetre pressure of mercury. The curves for zinc and cadmium are not parallel.

* *Proceedings of the Royal Society*, 1913, vol. lxxxix.-A, p. 58.
† *Transactions of the Chemical Society*, 1913, vol. ciii. p. 1534.

ELECTRO-METALLURGY.

CONTENTS.

I.—*ELECTRIC REFINING.*

Copper Refining in Kischtim, Russia.—An account of the electrolytic refining of copper in Kischtim is given by Professor Asejeff.* The black copper from the basic converters is melted in regenerative furnaces, refined and poled in the ordinary way, and cast into anode slabs weighing 82 to 90 kilogrammes by the aid of a casting machine. These anodes contain 99·6 per cent. of copper. There are 396 lead-lined wooden tanks, 1·84 metres deep, 1·19 metres wide, and 3·04 metres long, each bath containing 9 anodes and 10 cathodes. The current density is 200 amperes per square metre, which it is intended to increase to 400 or 500. The electrolyte, of specific gravity 1·2, contains 13–15 per cent. of crystallized copper sulphate and 10 per cent. of sulphuric acid, kept in circulation by a centrifugal pump. In order to check the increase in concentration of the copper sulphate, a few baths are provided with lead anodes. Cathodes remain in the bath about two weeks, anodes about a month. After the second and third days the cathodes are removed for straightening, and replaced.

The remains of the anodes requiring remelting amount to 12–18 per cent. The slime is washed, freed from lumps of copper, and is then boiled with sulphur, dried, and exported to England. This slime contains 3·6 to 4·6 per cent. of gold, 26·8 to 38·3 per cent. of silver, and 9 to 35 per cent. of copper. The present output of electrolytic copper (99·92 per cent.) is 16·4 tons per 24 hours, but this will shortly be doubled.

Electrolytic Lead Refining.—John F. Miller † gives an account of the process in use at the electrolytic lead refinery of the Consolidated

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* *Metall und Erz*, 1913, vol. x. p. 108.
† *Metallurgical and Chemical Engineering*, 1913, vol. xi. p. 463.

Mining and Smelting Company of Trail, B.C. The article is an abstract of a paper read before the Western Branch of the Canadian Mining Institute. The base lead bullion produced in the blast-furnace contains about 97 per cent. of lead, the remaining 3 per cent. consisting of gold, silver, antimony, arsenic, copper, zinc, and traces of other metals. This lead is cast into anode bars weighing about 400 lb. each. The tanks are 7 feet 4 inches long, 2 feet 6 inches wide, and 3 feet 8 inches deep, holding 20 anodes placed $4\frac{1}{8}$ inches between centres. The cathodes are sheets of pure lead placed between the anodes. The electrolyte contains 12 per cent. of hydrofluosilicic acid and 6 per cent. of lead fluosilicate. To prevent the deposition of soft, spongy lead and short circuiting of the tanks, glue is added to the electrolyte in the proportion of $\frac{1}{2}$ to 1 lb. per ton of lead produced. The rate of circulation of the electrolyte through the tanks is 35 cubic feet per hour. Two sets of cathodes are used, the first being removed after five days, and the second when the anodes are reduced to about 15 per cent. of the weight of the original anodes. The anode scrap is then also removed to a melting-pot to be again cast into anodes. The anode slime contains gold, silver, copper, antimony, and arsenic. The gold, silver, and copper (as blue vitriol) are recovered, but the recovery of antimony and arsenic has for the present been abandoned owing to their lower percentage in the slime and lower market price. The composition of the refined lead is given as—

								Per Cent.
Lead .	.	.	.	.	.	.	.	99·9938
Zinc .	.	.	.	.	.	.	.	0·0005
Silver .	.	.	.	.	.	* .	.	0·0013
Copper	.	.	.	.	.	.	.	0·00075
Iron .	.	.	.	.	.	.	.	0·00075
Tin .	.	.	.	.	.	.	.	0·0001
Antimony .	.	.	.	.	.	.	.	0·0028
Arsenic	.	.	.	.	.	.	.	Nil
Bismuth	.	.	.	.	.	.	.	Nil

II.—*ELECTRIC SMELTING.*

Calcium and its Alloys.—The lowering of the melting point of calcium chloride by alkali salts, which has usually been regarded as impracticable, as the alkali metal was then deposited alone, has now been shown by W. Moldenhauer and J. Andersen * to be quite practicable. Using the ordinary apparatus, in which the cathode is gradually raised, an electrolyte containing 85 per cent. of calcium chloride and 15 per cent. of potassium chloride yields calcium containing no more than traces of potassium. The current density must not be too low (60–110 amperes per square centimetre) and a current-efficiency of 75 per cent. is obtained. The potassium chloride may even be increased to 25 per cent.

* *Zeitschrift für Elektrochemie*, 1913, vol. xix. p. 444.

Alloys of lead or zinc with calcium may also be prepared with the same electrolyte, without potassium being deposited.

Electro-Metallurgy of Aluminium.—The nature of the electrolyte used in the production of aluminium has been further investigated by P. Pascal and A. Jouniaux,* the ternary system cryolite-alumina-fluorite being submitted to thermal study. The following melting points are found: cryolite 977°, fluorite 1361°, cryolite-fluorite eutectic 905° (74·6 per cent. cryolite), cryolite-alumina eutectic 904° (24 per cent. alumina), fluorite-alumina eutectic 1270° (26·9 per cent. alumina). Solid solutions are formed in every case up to near the eutectic composition. The ternary eutectic point is at 868°, the composition of the mixture being cryolite 59·3 per cent., fluorite 23·0 per cent., alumina 17·7 per cent. The determinations were not controlled by means of the microscope.

Yet another study of this electrolyte is due to R. Lorenz, A. Jabs, and W. Eitel,† who find that the system cryolite-alumina has a eutectic point at 937° and 32 molecular per cent. of alumina. Cryolite can retain as much as 20 molecular per cent. of alumina in solid solution. This result is confirmed by micrographic examination. The eutectic point of cryolite and sodium fluoride is at 23 molecular per cent. of cryolite and 886°. Solid solutions are formed at the sodium fluoride end of the system.

III.—*ELECTRO-DEPOSITION.*

Effect of Colloids on Electrolytic Deposition.—In a series of experiments, R. Marc ‡ shows that the action of colloids on electrolytic deposition is twofold. The influence on the coherence of the deposit is quite distinct from that on the size of the crystals. Electrolytes which have a tendency to deposit very large crystals require a large addition of colloid to reduce the size, and then considerable brittleness is usually produced. With baths containing colloids, relatively large lead crystals may be obtained which show the Brownian movement. Many photomicrographs of lead and zinc crystals from different baths are given.

Electro-Deposition in 1912.—A review of the progress in this branch is given by K. Neukam.§ The processes described are mainly from the patent literature, and relate to the production of denser deposits at the cathode, improvements in the composition of the anodes, the deposition of zinc, and the electrolytic refining of metals.

ANALYSIS AND PYROMETRY.

CONTENTS.

I.—*ANALYSIS.*

Aluminium.—The analysis of aluminium is discussed by J. Czoch-ralski.* The metal (2 grammes) is best dissolved in a mixture of 40 cubic centimetres concentrated sulphuric acid, 40 cubic centimetres water, and 2 cubic centimetres nitric acid, diluting to 300 cubic centimetres with cold water when all dissolved, and warming to coagulate the silica, which is collected and weighed as such. Should graphitic silicon be present, it is detected on dissolving the ignited residue in hydrofluoric acid, when the graphitic scales are easily recognized. The filtrate is treated with hydrogen sulphide to eliminate metals of that group (mainly copper and lead), and then with tartaric acid and ammoniacal ammonium sulphide to precipitate iron, nickel, and manganese. Magnesium may then be estimated in the final filtrate. Zinc is separated from iron, nickel, &c., by precipitating the latter with sodium hydroxide after oxidation with bromine, followed by electrolysis from an alkaline cyanide solution.

Iron and antimony may be detected microscopically in aluminium.

Bronzes.—An analytical method devised by W. Gemmell † allows of the analysis of tin-bronzes without first separating the tin with nitric acid, a process which always leads to a certain amount of iron and copper being retained by the tin oxide. The method depends on keeping tin in solution whilst copper is precipitated electrolytically. Two grammes of the alloy are dissolved in 20 cubic centimetres of a mixture of equal volumes of concentrated nitric and sulphuric acids, with 30 cubic centimetres of water. After boiling to expel oxides of nitrogen, the solution is cooled and diluted with 50 cubic centimetres of water. The copper is electrolytically deposited, preferably with rotating platinum gauze electrodes. When all is deposited, the solution is removed and re-

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* *Zeitschrift für angewandte Chemie*, 1913, vol. xxvi. p. 501.
† *Journal of the Society of Chemical Industry*, 1913, vol. xxxii. p. 581.

placed by 2 per cent. sulphuric acid, rotation being continued. The electrodes are then rinsed with water and alcohol and dried. The copper is pure and quite free from tin. Lead does not interfere, but is partly deposited as peroxide on the anode and partly precipitated as sulphate. If lead is to be estimated, from 5 to 10 grammes of the alloy are dissolved as above and evaporated until the sulphuric acid begins to fume. It is then diluted to 25 per cent. strength, boiled, and again diluted until it contains 7 per cent. of sulphuric acid by volume. The lead precipitate is quite free from tin.

Tin may be estimated in the solution remaining after electrolysis in one of two ways. The solution is diluted to 500 cubic centimetres and boiled, when the tin oxide is precipitated, filtered through a double Swedish filter paper, and washed with 1 per cent. sulphuric or nitric acid. Or the solution, immediately after removal of copper, is poured into cold 2 per cent. sulphuric acid saturated with hydrogen sulphide. After boiling for a few minutes the tin sulphide is collected, washed with a similar solution, dissolved in ammonium sulphide, and electrolyzed.

The filtrate from the tin is boiled down, the iron oxidized, and iron and nickel precipitated together by means of hot sodium hydroxide. The precipitate is redissolved in hydrochloric acid, the iron precipitated by ammonia and ammonium chloride, and nickel precipitated from the filtrate by dimethylglyoxime.

Zinc may be estimated in the final filtrate by evaporating with sulphuric acid, adding an excess of sodium hydroxide, acidifying with acetic acid, and electrolyzing.

Copper in Roasted Pyrites.—The following method for the estimation of copper in roasted pyrites is recommended by H. Koelsch.* A large quantity of the material (10 grammes) is dissolved in 40 cubic centimetres of strong hydrochloric acid, with 6 to 7 grammes of sodium hypophosphite. The hot liquid, without being filtered, is diluted with 100 cubic centimetres of hot water and 50 cubic centimetres of a 4 per cent. solution of sodium sulphide. The precipitate is collected, washed, and dissolved in nitric acid, which is then expelled by heating with sulphuric acid. The copper is then estimated electrolytically or by the iodine method.

Electro-Analysis of Copper Alloys.—A method of electro-analyis of brasses and bronzes is given by J. G. Fairchild.† Stationary electrodes, the cathode being a dish and the anode a spiral, are employed. It is claimed that a bronze analysis may be completed in about one day.

Electrolytic Analysis of Dross.—For the analysis of dross from tin or solder, L. Bertiaux ‡ recommends fusing with sodium carbonate and sulphur, extracting with water, and taking a part of the filtrate repre-

* *Chemiker Zeitung*, **1913**, vol. xxxvii. p. 753.
† *Metallurgical and Chemical Engineering*, 1913, No. 7, vol. xi. p. 380.
‡ *Annales de Chimie analytique*, 1913, vol. xviii. p. 217.

senting 1 gramme of the material. This solution is evaporated with
ammonium sulphate, oxidized with nitric acid, evaporated with sulphuric
acid until it fumes, and boiled with hydrochloric acid and ammonium
oxalate, the tin then being deposited electrolytically at 40°.

The lead in the undissolved sulphide from tin dross is washed, boiled
with a mixture of copper nitrate solution and nitric acid, and filtered.
The lead is then deposited electrolytically as peroxide. Solder dross or
lead dross is analyzed by treating 1 gramme with 100 cubic centimetres
of copper nitrate solution, and 25 cubic centimetres of nitric acid, diluting
to 300 cubic centimetres and electrolyzing.

Electrolytic Deposition of Antimony.—The use of ammonium
polysulphide as an electrolyte is recommended by N. K. Chaney.* The
antimony precipitate is dissolved in the smallest possible quantity of
ammonium polysulphide, from which free sulphur has been previously
removed by filtration. The solution is electrolyzed at the boiling point,
the initial voltage being 3·5 and the current density 1 ampere per square
decimeter, using a rotating anode. Deposition is complete in an hour,
and the deposit is bright like platinum and unlike the usual dark
antimony deposit. The boiling is necessary, as metallic antimony is
appreciably soluble in ammonium polysulphide, so that it is necessary to
destroy the greater part of the electrolyte. The solution at the end
should be colourless. Tin comes down together with antimony.

The results with lactates, tartrates, or calcium sulphide as electrolyte
are always too low.

Electrolytic Estimation of Copper in Brass.—For this estima-
tion B. Koch † recommends dissolving 1 gramme of turnings in 10 cubic
centimetres of nitric acid (1 : 1), diluting with 125 cubic centimetres of
water, adding 15 cubic centimetres of dilute sulphuric acid (1 : 1), and
electrolyzing with gauze electrodes, using 3 amperes and 3·5 volts at
70° to 75.° Deposition is then complete in an hour, and the electrodes
may be then rinsed without interrupting the current, washed with
alcohol, and dried.

Estimation of Copper by Electrolysis.—The difficulty of de-
positing the whole of the metal in the electrolysis of copper in solutions
containing nitric acid is attributed by J. H. Stansbie ‡ to nitrous acid,
which if not present in the first instance is produced during electrolysis
by reduction of nitric acid. A coating of copper was deposited on a
platinum cathode, which was then immersed in 50 cubic centimetres
HNO_3 (specific gravity 1·108), containing about 10 grammes HNO_3 and
less than 0·0001 gramme of HNO_3. Kept stationary for one hour, the
weight of copper removed was 0·7806 gramme. Rotated for a similar
period, the loss was only 0·0065 gramme. The rotation, by preventing

* *Journal of the American Chemical Society*, 1913, vol. xxxv. p. 1482.
† *Chemiker Zeitung*, 1913, vol. xxxvii. p. 873.
‡ *Transactions of the Faraday Society*, 1913, vol. ix. (1 and 2), pp. 11-13.

concentration of nitrous acid near the surface of the metal, accounts for the greatly diminished rate of solution.

Before the introduction of the rotating cathode the method adopted was to evaporate the nitric acid solution with sulphuric acid before electrolysis, as it was found impossible to deposit the whole of the metal without getting rid of the nitric acid, on account of the low current density used. But with the rotating cathode it is sufficient to keep the nitric acid low and add from 2 to 3 cubic centimetres of strong sulphuric acid. The usual plan is to dissolve about 0·5 gramme of the metal in 10 cubic centimetres of 1·2 nitric acid, boil down to decompose nitrites, and make up to 100 cubic centimetres with addition of 2 cubic centimetres of concentrated sulphuric acid. After forty minutes' electrolysis the exhausted solution will very rarely give any colouration with sulphuretted hydrogen.

The action of the sulphuric acid is probably twofold : (*a*) its ions help to carry the current and thereby check the formation of nitrous acid ; (*b*) it unites with nitrous acid to form a nitro compound which is much less effective in bringing about re-solution of the metal.

In a further paper dealing with this subject, E. Gilchrist and A. C. Cumming* point out that in the electrolysis of copper in solutions containing nitric acid using stationary electrodes, it is impossible under ordinary conditions to deposit the last two or three milligrammes of copper, but that the addition of urea overcomes that difficulty. The following results are given in support of the view that the urea acts by destroying the nitrous acid. Thin weighed sheets of copper of equal size were immersed for three hours in dilute nitric acid containing 10 cubic centimetres HNO_3 (specific gravity 1·42) per 100 cubic centimetres, and various amounts of nitrous acid, additions of urea being made in three cases.

†Nitrous Acid. Milligrammes per 100 Cubic Centimetres.	Urea. Grammes per 100 Cubic Centimetres.	Weight of Copper Dissolved (Milligrammes).
0·06	...	2·5
0·06	2	0·8
1·5	...	25·0
0·1	...	4·5
3·0	...	140·0
3·0	1	0·8
31·0	...	240·0
31·0	2	1·0

† Amount present *before* addition of the urea.

The following results were obtained with stationary electrodes in the presence of as much as 10 cubic centimetres concentrated nitric acid per 100 cubic centimetres :—

Copper present = 0·5080 gramme.

* *Transactions of the Faraday Society*, 1913, vol. ix. (1 and 2), p. 186.

(1) 100 cubic centimetres of solution containing 10 cubic centimetres of nitric acid and 5 grammes urea. Potential difference about 2·8 volts. Current (3 amperes) passed for three hours. Copper found = 0·5009 gramme. Error + 1 milligramme.

(2) 100 cubic centimetres of solution containing 10 cubic centimetres nitric acid. Current (3 amperes) passed for two hours without urea; then added 2 grammes urea and passed current again for one hour. Potential difference from 2·5 to 2·8 volts. Copper found = 0·5080 gramme. Error less than 1 milligramme.

Electrodes in the above experiments consisted of a platinum basin as cathode with a perforated platinum disc as anode.

Estimation of Mercury. — A method of analysing minerals and compounds of mercury by the dry method is described by A. C. Cumming and J. Macleod,* and results are given indicating the degree of accuracy obtainable.

The material to be analysed is heated with a mixture of iron filings and quicklime in a specially shaped glass bulb tube fitted with an asbestos filter. The mercury is deposited on the cooler portions of the tube. The methods of manipulation to obtain the best results are carefully described.

Estimation of Small Quantities of Lead. — The precipitation of lead as molybdate is recommended by A. V. Elsden and J. F. Stansfield † when the metal is only present in minute quantities. To the solution to be tested is added ferric chloride solution containing at least ten times as much iron as there is likely to be lead present. Ammonia is added in excess, and the solution is boiled and filtered. The precipitate is redissolved in hydrochloric acid, and ammonia is added until a slight permanent precipitate is obtained. Semi-normal hydrochloric acid is then added at the rate of 2 cubic centimetres for every 0·01 gramme of iron used, and the solution is reduced by sodium sulphite crystals. Without boiling off sulphur dioxide, 10 to 20 cubic centimetres of 10 per cent. ammonium acetate are added, and then 10 to 20 cubic centimetres of 5 per cent. ammonium molybdate. After boiling for a short time the precipitate is collected, washed with boiling water, redissolved in concentrated hydrochloric acid, a little tartaric acid and litmus added, just neutralized with ammonia, and acidified with a few drops of hydrochloric acid. After adding ammonium acetate the solution is boiled, and the precipitate collected, washed, dried, and weighed.

The method works well for alloys, such as brass and phosphor-bronze, containing less than 1 per cent. of lead.

Estimation of Zinc as Pyrophosphate.—The estimation of zinc as phosphate has been examined by T. M. Finlay and A. C. Cumming, ‡ this method having been found to give variable results. In the presence

* *Transactions of the Chemical Society*, 1913, vol. ciii. p. 513.
† *Ibid.*, p. 1039.
‡ *Ibid.*, p. 1004.

of sodium and potassium salts, double salts are formed, which are only slowly decomposed on washing. Microcosmic salt gives inaccurate results unless the solution is very carefully neutralized or slightly acidified with acetic acid after precipitation. If sodium salts are present, ammonium phosphate is added to the neutral solution, together with a large excess of ammonium chloride. This is less successful in presence of potassium salts, when a double precipitation in presence of ammonium chloride is necessary. The precipitate is ignited and weighed as pyrophosphate.

Iodometric Estimation of Copper.—The interference of nitrous acid in this estimation is avoided by M. E. Pozzi-Escot,* by adding an excess of urea. Ammonia is then added to remove other metals, and after redissolving the precipitate in sulphuric acid and reprecipitating, the united filtrates are acidified with acetic acid and titrated as usual.

Precipitation of Magnesium.—A note by Dr. Lindt † recommends the use of free orthophosphoric acid of specific gravity 1·30. for the precipitation of magnesium. One to five cubic centimetres of this acid, according to the quantity of magnesium present, are added to the cold ammoniacal solution, stirring thoroughly. The precipitate is always micro-crystalline, settles rapidly, and does not adhere to the side of the vessel.

Separation of Cadmium from Zinc.—Two methods of separation are described by W. D. Treadwell and K. S. Guiterman.‡ One consists in precipitating cadmium by hydrogen sulphide from a hot solution containing $5N$ sulphuric acid by continuing to pass the gas until cold. If the zinc be in very large excess, it may be necessary to reprecipitate. The second method consists in mixing one gramme of the chlorides or sulphates with 8 grammes of potassium oxalate, 2 grammes of ammonium oxalate, and 0·3–0·5 gramme of oxalic acid. The cadmium is deposited electrolytically, using gauze electrodes at 70°–80°, and about four hours are required for each 0·1 gramme of cadmium.

Stereoscopic Microscope.—A new metallurgical microscope for stereoscopic vision is described.§ This is made by Messrs. Leitz to the specification of Wesley Lambert, and is adapted for the examination of fractures, and of samples which have not necessarily been subjected to previous polishing or etching. Focussing correction may be made for each eye-piece separately, and the instrument may be used horizontally or vertically.

The lens-holding portion of the apparatus may be turned through 180° to render possible the examination of objects too bulky to be placed upon the stage. Three sets of paired objectives are supplied of 24 millimetres,

* *Annales de Chimie analytique*, 1913, vol. xviii. p. 219.
† *Metall und Erz*, 1913, vol. x. p. 420.
‡ *Zeitschrift für analytische Chemie*, 1913, vol. lii. p. 459.
§ *Metal Industry*, 1913, vol. v. p. 298.

40 millimetres, and 48 millimetres focus respectively. A small lamp is fitted in a good position for working under oblique illumination, whilst the mechanical stage is so arranged that the instrument may also be used for transmitted light when desired.

Stolberg Laboratory for Electro - Analysis. — An electro-analytical laboratory at the Stolberg Lead and Zinc Company's works is described by H. Nissenson.* The arrangement of benches and connections is a convenient one, and provides for all the ordinary operations with either stationary or rotating electrodes, very little space being occupied.

Titration of Copper with Methanal-Sulphurous Acid.—A paper by P. Malvezin † recommends the use of methanal-sulphurous acid, prepared by saturating commercial formaldehyde with sulphur dioxide, as a volumetric reagent for copper. The solution is standardized by means of pure copper. No indicator is required. The copper solution to be tested is made ammoniacal, and the standard solution is run in until the deep blue colour changes to green, and then suddenly disappears. Very small quantities of copper may be estimated in this way.

Volumetric Apparatus.—An apparatus for preserving the constant titer of standard solutions is described by Dr. Lindt.‡ It differs very little from other apparatus for the same purpose. The siphon tube, provided with a screw clip, enters the burette just above the tap. The large reservoir bottle is connected with a second small bottle, through which all entering air has to pass, and into which solution can escape if the main bottle becomes warm.

Volumetric Estimation of Gold.—V. Lenher § recommends the titration of gold chloride solutions by means of sulphurous acid, standardized with iodine. An excess of magnesium chloride is added to the gold chloride solution, and sulphurous acid is run in until the yellow colour disappears. No other indicator is necessary.

Zinc Sulphide Precipitates.—It has been found by K. Bornemann ‖ that precipitates of zinc sulphide may be quite accurately roasted directly to oxide. The filter-paper is best incinerated in an open porcelain crucible. The ignition of the precipitate may be carried out in a closed platinum crucible, 15 to 20 minutes over a Teclu or Méker burner being sufficient to destroy all sulphate. A porcelain crucible may be used in a muffle with oxidizing atmosphere, or in an electric furnace, a temperature of 950° being desirable.

* *Metall und Erz*, 1913, vol. x. p. 119.
† *Bulletin de la Société chimique*, 1913, Ser. iv., vol. xiii. p. 721.
‡ *Metall und Erz*, 1913, vol. x. p. 139.
§ *Journal of the American Chemical Society*, 1913, vol. xxxv. p. 733.
‖ *Zeitschrift für anorganische Chemie*, 1913, vol. lxxxii. p. 216.

The difficulty of filtering zinc sulphide is completely overcome by the addition of sulphur. An acetic or chloro-acetic acid solution is used, and the sulphur is precipitated by passing hydrogen sulphide through sulphurous acid, or by adding sodium bisulphite to the solution about to be precipitated. The two colloids coagulate one another, and the precipitate is easily collected.

II.—PYROMETRY.

Cold - Junction Correction in Thermocouples. — Expressions giving true and approximate values for the corrections which must be applied to the indications of thermocouples when the temperature of the cold-junction is other than zero are derived by P. D. Foote.* The correction to be applied depends not only on the temperature of the cold-junction but also on that of the hot-junction, *i.e.* on the temperature which the instrument is measuring. The lower the temperature under observation, the greater the correction necessary for variations in cold-junction temperature. Curves illustrating this for a Pt — PtRh (10 per cent.) couple are given. Various compensating and other devices are in use for the purpose of eliminating cold-junction correction. One form, devised by the Bristol Co., U.S.A., depends for its action on the change in resistance of a loop of platinum wire dipping into mercury, and placed in circuit close to the cold-junction. The expansion and contraction of the mercury short-circuits varying lengths of the wire. Crompton instruments are provided with a multiple scale, each scale corresponding to a definite cold-junction temperature. One of the simplest of these devices is that of Siemens and Halske, in which the instrument is provided with a large zero adjustment so constructed that the pointer can be set on open circuit to a temperature corresponding to that of the cold-junction. Compensating devices are not to be recommended; they are cumbersome and liable to error. The temperature coefficient of some galvanometers is so large that errors due to changes in surrounding temperature may be as large as those due to the cold-junction. The proximity of other magnetic instruments or of iron must also be guarded against. Attention to the above sources of error, an occasional verification of the thermocouple calibration, and proper correction for cold-junction temperature are advised.

Foundry Pyrometers.—H. W. Gillett † describes existing forms of pyrometers, and discusses their relative merits for foundry purposes.

The importance of an exact knowledge of pouring temperature and of furnace temperature is dealt with, and it is shown that some method of standardizing these variables is essential when the foundryman is experimenting to find the best alloy for a given purpose.

* *Metallurgical and Chemical Engineering*, 1913, vol. xi. (No. 6), pp. 329–333.
† *Metal Industry*, 1913, vol. v. pp. 103–104, 140–143.

For general use in the foundry, optical pyrometers are unsuitable except in special cases because their lower limit of utility is above the melting point of a large number of alloys. This objection is overcome to some extent in the radiation type of pyrometer such as the Fery, Brown, and Thwing instruments, but all the above devices, in common with the optical types, are standardized to read "black body" temperatures, and the readings obtained from the surface of molten metal in the crucible are, on this account, subject to very considerable corrections which will vary with the nature of the alloy and the thickness of the oxide film. A further source of possible error lies in the fumes given off by brass and similar alloys, but this is not mentioned by the author. The chief advantage of the radiation pyrometer lies in the fact that it has never to be in actual contact with the work.

The various types of thermo-electric instruments are described, using base metal couples of iron with alloys of iron-aluminium, nickel-copper, nickel-chromium, nickel-aluminium, or pure nickel. In many kinds of commercial pyrometers the galvanometer needle has a zero adjustment, and this may be used to correct for cold-junction temperatures. Other possible sources of error and their remedies are touched upon.

Heating and Cooling Curve Recorders.—An apparatus has been placed on the market by the Leeds Northrup Co. which autographically records differential heating and cooling curves.* The spot of light from the galvanometer connected to the differential couple is thrown on to a movable scale carrying the pen. This scale is moved to right or left so as to follow the movements of the spot, thus drawing the pen horizontally across the drum carrying the sectional paper. The temperature is measured by means of a potentiometer whose slide wire is wound on the drum. The spot of light from the temperature measuring galvanometer is kept stationary on a second *fixed* scale by revolving the drum whereby the point of contact on the slide wire is altered so as to keep the electromotive force balance. The revolving of the drum gives the pen its vertical movement.

Improved Optical Pyrometer.—Successive improvements in the Wanner type of optical pyrometer, fitting it more perfectly for industrial use, are described by C. G. Fisher.† In this instrument the temperature of an object is determined by comparing a certain portion of the visible radiation emanating from it with that of a standard. The latest improvement consists of a direct reading open-temperature scale due to G. A. Shook for the correct determination of the temperature of materials when *not* under "black-body" conditions, *i.e.* such objects as molten metal in pots and ladles, billets, material passing through rolls, &c. The first scale perfected was one for iron and steel. A different scale is required for each material. This instrument, known

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* *Metallurgical and Chemical Engineering*, 1913, vol. xi. No. 4, p. 221.
† *Ibid.*, No. 9, pp. 532–533.

as the "New Scimatco" optical pyrometer, can be obtained from the Scientific Materials Co., of Pittsburg, U.S.A.

Modern Methods of Temperature Measurement.—The subject is fully dealt with in three articles by R. S. Whipple.*

Expansion Thermometers.—The use of a glass bulb and capillary, containing alcohol and an arbitrary scale, is due to Galileo. Hooke, in 1681, suggested the melting point of ice and boiling point of water as fixed points. In 1714 Fahrenheit suggested his scale. With increased accuracy it was early realised that secular change in the glass was responsible for serious errors. At the Reichsanstalt, Berlin, the Jena glasses have been found most satisfactory. Their price is rather higher, but it is wise to insist on them, as the zeros are much more constant than with ordinary English glass. It is possible with high-grade thermometers to measure the temperature accurately throughout the range to 0·001° C. Practically any range of openness of scale and reasonable length is obtainable by insertion of small chambers at required points in the capillary.

By the introduction of an inert gas under pressure over the mercury an increase up to 540° C. is possible.

Special mountings and tube-protecting devices, fitting thermometers for rough and tumble requirements of engineers, are described.

Thermometers having an envelope of quartz with mercury under pressure have been developed in Germany, which can be used up to 700° C. Tin has been substituted for mercury, and such thermometers have been used up to 1000° C. For very low temperatures such as liquid air, petrol in glass or quartz may be used.

It is possible to electrically record at a distance the readings of mercury thermometers by means of the changes in the apparent resistance of a high-resistance bronze wire stretched from the bottom of the bulb along the capillary. Metal tubes have been substituted for glass. Mercury in steel thermometers, due to the Bristol & Taylor Instrument Company, consisting of a steel bulb attached to a steel capillary tube connected to a form of Bourdon pressure gauge, the recording mechanism of which may be up to 75 feet from the bulb, may be relied on up to 540° C. (1000° F.).

Thermo-Electric Thermometers.—In 1882 Seebeck made the discovery that when a junction of two dissimilar metals is heated an electromotive force is generated. Becquerel proposed this method for measuring temperatures, and employed a platinum-palladium couple ; his son pointed out the importance of using a galvanometer of high resistance. The above couple proved unreliable, and Barns and Tait proposed platinum-platinum-iridium (10 per cent.). Le Chatelier showed that platinum-platinum-rhodium (10 per cent.) was more stable above 1000° C., and adopted this couple as standard. His work has since been confirmed, most recently at the Geophysical Laboratory, Washington.

Difficulty in the production of standard ingots of platinum-iridium

* *Engineer*, 1913, vol. cxvi. pp. 129–130; pp. 157–158; and pp. 183–184.

and platinum-rhodium have now been overcome, notably by Messrs. Heræus and Johnson Matthey & Co., and it is now possible to rely upon successive batches of couple wire of these alloys giving the same electromotive force at the same temperature.

The most satisfactory of the so-called " base " metal couples introduced of recent years is the silver-constantan (Cu 60, Ni 40 per cent.), with an upper limit of 600° C. For temperatures from 700–1000° C. the Hoskins couple—nickel–nickel-chromium (10 per cent.)—may be used.

The control of the temperature of the " cold-junction," as it is called, has been the bugbear of pyrometry. The maintenance of a fixed and definite temperature of the cold-junction by immersion in ice is impracticable industrially, and of the various means devised for overcoming the difficulty the most satisfactory is one originally due to Bristol, suggested independently by Peake, consisting in the use of compensating leads of an alloy such as copper-nickel of such composition as to give the same electromotive force against copper as that given by the platinum-platinum alloy. The compensation so obtained is correct to within 10 per cent. up to temperatures of 300° C.

Direct and potentiometric methods of measuring the electromotive force of thermocouples are discussed, together with autographic recording instruments. The *modus operandi* of thread recorders, including the Darwin double-thread recorder, is described. An effective semi-automatic recorder, due to H. Brearley, enables cooling and heating curves and critical points to be rapidly obtained.

Resistance Thermometers.—Sir W. Siemens in 1871 first suggested the change in electrical resistance of a wire with temperature as a means of measuring temperature; Callendar and Griffiths in 1887 made the method reliable. The theory of the method is given, and the mode of measuring the resistance, generally by the ordinary Wheatstone bridge, dealt with. The first and most successful recorder for use with this method, and due to Callendar, is described. The upper limit of resistance thermometers is 1200° C.

Thermocouples can rarely be employed above 1400° C. because of the difficulty of finding a gas-tight envelope to protect the junction. Tubes of a material called " Marquardt " have recently been introduced by the Royal Berlin Porcelain Manufacturing Company, which will resist temperatures up to 1700° C. The material is, however, very brittle and sensitive to sudden changes of temperature.

Optical and Radiation Pyrometers.—Although E. Becquerel had proposed in 1864 to refer the measurement of high temperatures to the measurement of the intensity of red radiations emitted by incandescent bodies, it was not until Le Chatelier invented his optical pyrometer in 1892 that any really satisfactory attempt was made to determine the temperature of a hot body by measuring the radiation emitted from it. This instrument, modified by Féry, is still one of the most useful. The theory underlying this method is given. The various optical and radiation instruments are described with the aid of drawings and photographs. Finally, suggestions are made with a view to aiding those considering

the installation of temperature measuring instruments for purposes' of steam plant, cold storage, casting temperatures, heat treatment of metals (one of the greatest fields for pyrometric work), brick and porcelain works, &c.

Standardization. — Useful and satisfactory points for calibrating thermocouples are as follows :—

	Temp. ° C.
Tin, freezing point	. 231·92
Lead, freezing point	. 327·43
Zinc, freezing point	. 419·37
Sulphur, boiling point	. 444·70
Antimony, freezing point	. 630·70
Sodium Chloride, freezing point	. 800·00
Silver, freezing point	. 960·98
Copper, freezing point	. 1083·00

Temperatures in a Silicon Carbide Furnace.—Results are given of pyrometric experiments by L. E. Saunders * on a Crystolon (silicon carbide) furnace. The furnace was of brick, and contained a core of granular carbon which was surrounded by the charge mixture for making the carbide. A special double-walled, water-cooled graphite tube, 1 metre long and 76 millimetres internal diameter, closed at one end, communicated with the interior of the furnace and permitted observations with a Thwing radiation pyrometer to be made during the furnace run, which lasted forty hours. After opening up the furnace, the carbon core was found to be partly graphitized, and was surrounded by a layer of silicon carbide and an outer layer of " fire sand," or impure carbide. The values found include :—

	Degrees C.
Formation point of " fire sand "	. 1600 ($+50$)
Formation point of crystalline silicon carbide	. 1840 ($+30$)

Decomposition of the crystalline carbide takes place at 2240° C. (± 5).

* *Engineering*, vol. xcvi. p. 399.

FURNACES AND FOUNDRY METHODS.

Carbon-Tube Furnaces.—Improvements in this type are described by K. Friedrich.* The ordinary type has many inconveniences, and experiments have been made with the object of avoiding them. One furnace, taking about 700 grammes of metal, has a carbon tube 250 mm. long by 60 mm. bore, the walls being 10 mm. thick. This takes 400 amperes at 4 to 6 volts. A still larger pattern has a carbon tube 400 mm. long, 155 mm. bore, with walls 22 mm. thick, and takes several kilogrammes of metal. A further improvement is the enlargement of the ends of the tube, so as to make better contact with the flanges. The copper bands surrounding the flanges are now made hollow and water-cooled. The insulating material is protected by an iron casing, and the upper carbon surface is covered with carbon powder. It is possible, with the 700-gramme furnace, to keep temperatures above 1000° constant within 5°. A special current regulator is also described, consisting of a copper tube, 8 mm. outside and 6 mm. inside, 12·2 metres long, bent into 18 sections, and cooled by water. By shunting different sections out or in, a rough adjustment of the resistance is obtained, fine adjustment being brought about by varying the flow of water. Up to 1000 amperes at 8 volts may be passed, the cooling water then leaving at a temperature of 70°.

Cathode Ray Vacuum Furnace.—For the purpose of obtaining high temperatures in a very high vacuum, E. Tiede † has devised a furnace in which the heating is produced by cathode rays. A vertical glass tube is fixed in an iron stand. Within this is a brass tube, cooled internally by circulating water, and carrying the massive aluminium anode. A silica rod, fixed by means of a central hole in the anode, carries an outer porcelain crucible, within which is placed the crucible which actually holds the material. The enclosing vessel is a large silica bulb, ground into the lower glass part, to which the tube from the exhaust pump is attached. The aluminium cathode is carried by a brass tube forming an upper extension of the furnace. This part is also cooled by water. The main bulb is also provided with a side arm for visual observation, in case the bulb becomes coated with products of distillation.

* *Metall und Erz*, 1913, vol. x. p. 511.
† *Berichte der deutschen chemischen Gesellschaft*, 1913, vol. xlvi. p. 2229.

A coil, with 20 cm. spark and Wehnelt interrupter, is used, and it has been found possible to melt platinum, boron, and even (in small quantities) tantalum.

Efficiency of Electric Melting Furnaces.—The consumption of energy in electric melting furnaces is discussed by C. Hering.[*] Brass is taken as an example, and probable values are assumed for the energy required for melting and lost in the furnace walls and the electrodes. From the results, the conclusions are drawn that the energy consumption is less (*a*) the more rapidly the melting is done, and (*b*) the smaller the charge, and therefore the furnace.

The ideal melting furnace is one which melts as fast as it can be moved from mould to mould and poured. The idea is not impracticable for small brass castings, and possibly steel.

What would seem to be the best practice is a single small furnace melting a large number of charges in succession.

Electric Furnaces.—The first of a series of articles by W. McA. Johnson and G. N. Sieger [†] on the design, characteristics, and commercial application of electric furnaces, deals with the general principles of design and economics. Some practical types of furnaces are briefly indicated and discussed. Electrical heat must be applied efficiently. High voltage is a good commercial point. Electric heat is expensive, and can only be used where its efficiency is great, but if intelligently studied and applied, will become of large industrial importance, and existing electric furnace limits pushed to extremes not now thought possible.

Electrodes and Electrode Holders.—The principal types of electrode holders for electric furnaces are described,[‡] with additional notes on joining and dimensioning electrodes. The article is illustrated with a large number of drawings.

Furnace Temperatures.—G. Howell Clevenger,[§] using the Le Chatelier thermocouple, has determined the temperature attained in the case of a number of operations in the metallurgy of copper and lead. The average temperatures of two copper blast-furnaces running side by side, and making almost identical slags (SiO_2, 31 per cent.; FeO, 52 per cent.) were 1201° C. and 1207° C. respectively for a period of two weeks. The effect of temperature upon the rate of smelting is shown in the following table :—

* *Metallurgical and Chemical Engineering,* 1913, vol. xi. No. 4, pp. 183–187.
† *Ibid.,* vol. ix. No. 9, pp. 504–507.
‡ *Ibid.,* 1913, vol. xi. pp. 321–326.
§ *Ibid.,* 1913, vol. xi. pp. 447–449.

	Furnace Numbers.	
	1.	2.
	Degrees C.	Degrees C.
Smelting at a furious rate	1261	1255
Smelting at normal rate	1197	1227
Smelting very slowly (apparently lower limit) .	1123	1137

In the case of copper reverberatory furnaces, the following table gives the temperatures at various points along the centre line of three furnaces :—

	Furnace Numbers.		
	1.	2.	3.
	Degrees C.	Degrees C.	Degrees C.
Charging hole from front 1 . . .	1260	1308	1523
Charging hole from front 2 . . .	1305	1353	1594
Charging hole from front 3 . . .	1346	1449	1723
Charging hole from front 4 . . .	1339	1540	1723
Temperature of slag	1202	1290	1310
Melting point of slag	1190	1190	1285

The temperature of the gas in the flue of a reverberatory furnace was found to vary from 1300° C. at the furnace to 642° C. 120 feet from the furnace at the foot of the stack.

The average temperatures in copper-refining furnaces was found to be as follows :—

	Degrees C.
Charge melted and ready to rabble . . .	1141
After 25 minutes' rabbling	1103
After 75 minutes' rabbling	1103
At end of rabbling	1103
After 20 minutes' polling	1110
At end of polling	1117
Heated to	1125
After ladling 20 minutes	1121

And in the case of copper converters—

Matte introduced	1170
Turned down to skim	1297
Turned back to blow	1284
Cooling during skimming	13
Temperature of escaping gas at end of 10 minutes	1260
Temperature of escaping gas at end of 20 minutes	1270
Temperature of escaping gas at end of 30 minutes	1275
Temperature of escaping gas at finish . . .	1195

It was found that the temperature of the slag made in a lead blast-furnace smelting a given charge is remarkably constant, but irregular operation of the furnace is shown by a change in the mean temperature of the slag. According to composition, the mean temperatures of different slags vary from $1126°$ C. to $1180°$ C.

Figures are also given showing the variations in temperature in three types of roasting-furnaces, viz. long-hand reverberatory, Pearce turret and Herreshoff furnaces.

Fusibility of Refractory Oxides.—Using a carbon-tube vacuum furnace, O. Ruff, H. Seiferheld, and J. Suda * find that alumina is the only oxide with a melting point which is fairly independent of the nature of the atmosphere. It melts at $2010 \pm 10°$. Beryllium oxide, melting at about $2525°$, and zirconium oxide, melting at about $2585°$, are suitable for use as crucibles for very high temperatures, although the latter undergoes partial reduction in the carbon furnace. Magnesia is resistant, but volatilizes rapidly.

Lime forms carbide, but may be used when a good vacuum is kept. Thorium, yttrium, cerium, and chromium oxides form carbides even under a very low pressure. Titanium dioxide is reduced to a lower state of oxidation.

High-Pressure Furnace.—In the course of an investigation of boron compounds, A. Stähler and J. J. Elbert † have devised an electric furnace for experiments under high pressures. A heavy steel autoclave is used. The current enters by a phosphor-bronze tube, tightly packed in by vulcanized fibre packings. It then reaches the resistance tube, which is of carbon, and then passes through the outer wall of the auto-clave, which is connected with the other terminal. The carbon tube is surrounded by granulated wood-charcoal, contained in an asbestos cylinder. The substance to be heated is contained in a graphite crucible. The lower part of the autoclave stands in water, and water is continually poured over the upper part. As the thermocouple cannot be used beyond about $1500°$, a number of determinations of the temperature are made at different pressures and with different currents. The curve connecting temperature by heating current under constant pressure is practically a straight line, so that it is possible to extrapolate.

Pressures up to 500 atmospheres may be reached, and by passing 1000 amperes at 25–30 volts through a thin carbon tube, temperatures up to $1900°$ have been obtained. The furnace has been used for experiments on the extraction of nitrogen from the atmosphere by means of boron.

Melting Points of Fire-Bricks.—Recent estimations of the melting points of fire-bricks are described in Technologic Paper No. 10 of the Washington Bureau of Standards. ‡

* *Zeitschrift für anorganische Chemie*, 1913, vol. lxxxii. p. 373.
† *Berichte der deutschen chemischen Gesellschaft*, 1913, vol. xlvi. p. 2060.
‡ *Engineering*, 1913, vol. xcv. p. 677.

The method adopted was to heat the sample of refractory material in a graphite spiral resistance furnace working in a water-jacketed vessel, which was exhausted to a pressure of 2 millimetres of mercury. Temperatures were measured by an optical pyrometer of the Holborn-Kurlbaum type, which was calibrated by using the melting points of copper, silver, the copper-silver eutectic, and platinum as fixed points. The crucible employed for the platinum calibration was a double one, made of a mixture of magnesia and alumina supplied by the Königl. Porzellanmanufaktur, of Berlin. Trouble was experienced in the blackening of the fire-brick samples by the reducing gases generated inside the furnace-casing at high temperatures. This was met by placing the test-pieces on a bed of alundum at the bottom of a test-tube made of a mixture of 72 per cent. kaolin and 28 per cent. alumina, which melts at about 1800° C.; traces of oxygen were also introduced into the furnace whilst running, but the pressure was kept down to 2 millimetres as before. The usual duration of a test was half an hour, but some test samples were preheated to 1550° C. for six hours, and this treatment was found sometimes slightly to raise the ultimate melting point, which was regarded as the lowest temperature at which the sample under test was distinctly seen to flow.

The following table summarizes the results obtained :—

Material.						Lowest Temperature of Flow.
						Degrees C.
Silica	.	.	.	.	.	1750
Kaolin	.	.	.	.	.	1740
Bauxite brick		.	.	.	.	1790-1820 (some at 1600)
Alumina	.	.	.	.	.	2010
Magnesia brick	.	.	.	.	2165
Chromite brick	.	.	.	.	2050-2180

No definite relation was established between the melting point and composition of any fire-clay bricks.

Melting Points of Refractory Materials.—C. W. Kanolt * has succeeded in determining the melting points of several refractory oxides, using an Arsem electric graphite furnace and a Holborn-Kurlbaum optical pyrometer. It is not possible to melt either lime or magnesia in a vacuum, as they volatilize completely before melting. In such cases an atmosphere of hydrogen is used. Magnesia may be melted in a graphite crucible, but lime forms a carbide, and must be melted in a tungsten crucible, or without using a crucible, by moulding the lime itself into the form of a tube, through which hydrogen is passed. Alumina and chromium oxide may be melted in tungsten crucibles.

The melting points found are :—Magnesia, 2800°; lime, 2570°; alumina, 2050°; chromium oxide, 1990°.

Pressed Steel Melting Pots.—Pressed steel pots for melting soft metals or alloys, such as babbit metal and solders, are now manufactured by the Eclipse Fuel Engineering Company of Rockford, Illinois.* They are made in a number of sizes and shapes, and are conducive to more rapid melting on account of their thinness as compared with the thicker cast iron vessels usually employed. It is stated that they may even be economically employed for melting metals such as zinc or aluminium (which attack iron), since they are considerably cheaper than the cast iron pots, and the cost of replacing them when worn out is small.

Smelting Copper Mattes containing Lead.—A series of experiments by W. Menzel † show that, whilst it is impossible to separate lead and copper in a matte by smelting with sodium or calcium sulphate and carbon to obtain "tops" and "bottoms," good results are obtained by smelting with lime and carbon, the products being calcium sulphide and metallic lead. If an electric furnace be used, it must be of the resistance type, as an arc causes great losses of lead by volatilization. A furnace is described, designed for continuous working. The top is closed, with changing hoppers, and the carbon electrodes are at the ends of the hearth. As the crude lead is tapped off, together with the bulk of the matte, sufficient matte is left to conduct the current whilst fresh material is being charged in. Two movable subsidiary electrodes would be used in starting the furnace. In a trial with a small furnace, 20 kilogrammes of Otavi matte were smelted, with 2·4 kilogrammes of lime, and 400 grammes of coke, using 600 amperes at about 56 volts. About 70 per cent. of the lead sulphide is decomposed, the remainder combining with or dissolving in the calcium sulphide.

It is also practicable to smelt copper sulphide or matte to copper, by using lime and carbon.

Smelting Nickel Ores.—Improvements in the treatment of nickel ores and other products are described by H. Pedersen.‡ The separation of nickel and copper from iron is greatly facilitated by the use of electrical smelting. The matte is then roasted to sulphate, the iron becoming oxide, which is left in the residue on extraction with acid water. Only 80–90 per cent. of the nickel is thus extracted, but the residual iron oxide is a very convenient addition to the fusion for crude matte, as it assists in slagging the silicious gangue. It acts as an oxidizing agent.

$$FeS + 3Fe_2O_3 = 7FeO + SO_2.$$
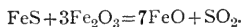
The last traces of iron are removed from the solution by adding nickel oxide and blowing air through, and copper and nickel are then separated in the wet way.

Shaft furnaces, with a carbon electrode at the base, give a better

* *Brass World*, 1913, vol. ix. p. 245.
† *Metall und Erz*, 1913, vol. x. pp. 193, 230.
‡ *Ibid.*, p. 384.

efficiency than trough furnaces with inclined electrodes. The best lining for the furnace, when the gangue is acid, is a poor ore, ground to powder and moistened, and mixed with lumps of the same ore, and then rammed into place. A rich ore conducts the current too well, and so cools the furnace. On the large scale, with the ore used, about 250 kilowatt hours should be required per ton of ore.

STATISTICS.

Gold Coast Gold Production in 1912.—The Secretary of Mines of the Gold Coast * reports the value of gold produced in the Colony in 1912 as the record figure of £1,499,469. The total weight of fine gold obtained was 352,957 ozs., one third of which was obtained from the mines on the conglomerate reef in the Tarquah district.

Indian Mineral Production in 1912.—The Director, Indian Geological Survey,† reports the following figures for the output of some of the minerals obtained in India in 1912.

	1911.		1912.	
	Amount.	Value.	Amount.	Value.
		£		£
Coal (tons) . . .	12,715,534	2,502,616	14,706,339	3,310,365
Gold (ozs.) . . .	583,567	2,238,143	590,555	2,271,806
Manganese ore (tons) .	670,290	648,801	637,444	884,404
Lead and lead ore (tons) .	35,361	181,989	25,739	153,069
Tungsten ore (tons). .	1,308	99,989	1,672	115,200
Tin and tin ore (cwt.) .	3,707	24,904	7,507	50,944
Silver (value) . . .	...	11,575	...	11,829
Chromite (tons) . .	3,804	5,072	2,890	3,849
Magnesite (tons) . .	3,490	1,047	15,379	4,614
Copper ore (tons) . .	2,238	3,404	9,619	13,709

Coal shows the most important rise in output of all the Indian minerals in 1912, the increase in production being 16 per cent. as compared with the previous year.

New Mexico Metal Production in 1912.—The production in 1912 was valued at 8,528,000 dols., an increase of 5,823,000 dols., as compared with last year.‡ The important feature of the year's production was the great increase in copper, chiefly due to the operations of the Chino Copper Company.

* *Board of Trade Journal,* 1913, vol. lxxxiii. p. 34. † *Ibid.,* p. 33.
‡ *Metallurgical and Chemical Engineering,* 1913, vol. xi. No. 8, p. 449.

New South Wales Mineral Output in 1912.—The Department of Mines New South Wales * reports the total value of the mineral output of the State during 1912 as £11,641,435, an increase of nearly two millions on the figure for 1911. The principal items of the production are given in the table below :—

	Quantity.		Value.	
	1911.	**1912.**	**1911.**	**1912.**
			£	£
Coal (tons)	8,691,604	9,885,815	3,167,165	3,660,015
Copper ingot, matte and ore (tons) .	12,100	11,034	590,102	579,791
Gold (ozs.)	181,121	165,295	769,353	702,129
Iron (tons)	36,354	32,677	145,416	130,708
Lead (tons)	17,276	17,251	209,784	264,530
Silver-lead ore, concentrates, &c. (tons).	338,468	345,307	2,265,669	3,229,614
Silver ingot and matte (ozs.) . . .	1,767,496	2,389,195	177,095	251,652
Oil shale (tons)	75,104	86,018	36,980	34,770
Tin ingot and ore (tons) . . .	1,929	2,074	307,089	338,074
Wolfram (tons)	283	172	29,991	16,584
Zinc metal and concentrates (tons) .	516,378	520,518	1,414,980	1,766,242

The tin mining industry, which largely consists in dredging operations, has been encouraged by the very high price of the metal. Considerable discoveries of lode tin ore are reported, and the results of a preliminary examination of this show the existence of considerable quantities of massive tin ore assaying 30–50 per cent. metal.

Ontario Mineral Output.—The following figures regarding the output of certain minerals by Ontario in the first half of 1913 have been published by the Ontario Bureau of Mines.†

	January-June 1912.		January-June 1913.	
	Quantity.	Value.	Quantity.	Value.
		Dollars.		Dollars.
Gold (ozs.)	11,854	235,198	106,091	2,171,147
Silver (ozs.)	14,258,403	7,936,600	13,890,692	7,693,713
Nickel (tons of 2000 lb.) .	10,179	2,166,895	12,104	2,514,414
Copper (ditto) . . .	5,170	736,469	5,873	832,645
Cobalt and Nickel Oxides, &c. (lb.) . .	854,324	192,073	404,060	186,347

1 Dollar = 4s. 1½d.

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* *Board of Trade Journal*, 1913, vol. lxxxiii. p. 91. † *Ibid.*, vol. lxxxii. p. 757.

Russian Platinum Industry.—The production of platinum in the Urals in 1912 was 337 pouds 8 funts, rather less than in 1911. A Bill to prohibit the export of crude platinum from Russia, with a view to encouraging the home refineries, is under the consideration of the Russian legislature.*

(40 funts=1 poud=526·645 ozs. Troy.)

Russian Poland Zinc Industry.—The amount of zinc smelted in Russian Poland in 1912 is reported as 1,328,329 pouds, as compared with 606,131 pouds in 1911, an increase of 119 per cent. The production of zinc dust in 1912 amounted to 40,357 pouds, an increase of 311 per cent. over the figure for 1911.† These are record increases.

1 Poud=36 lb.

Transvaal Gold Production.—The number of companies reporting to the Transvaal Chamber of Mines in November 1912 was 62. The total quantity of ore milled was 2,203,900 tons, and the yield 757,337 fine ounces gold.‡ The same number of companies reported in April 1913, the total quantity of ore milled being 2,356,204 tons, and the yield for the month 784,074 fine ounces gold.§

United States Production of Lead.—The amount of refined lead produced in the United States in 1912 is stated ‖ as 480,895 short tons showing a decrease of 1·2 per cent. on the output for 1911.

United States Production of Zinc in 1912.—The zinc output of the United States in 1912 is given as 338,806 net tons as against 286,526 tons in 1911.¶

These figures refer only to primary spelter smelted directly from ore.

Secondary spelter, recovered from dross and old metal, amounted to 53,300 tons in 1912.

United States Scrap Metal Treatment.—The recovery of metal from scrap is discussed,** the pure metal obtained being designated " secondary metal," as distinct from the primary metal smelted direct from the ore.

The value of a secondary metal is usually below that of the corresponding primary metal ; but the former has special applications in cases where the class of work requires the impurities which the secondary metal possesses but which are absent from the primary metal.

It is stated that there is a notable increase in the application of magnetic separation of iron filings from the metal scrap and also in the separation of moulding sand and cinders, the general tendency being

 * *Metal Industry*, 1913, vol. v. p. 211.
 † *Board of Trade Journal*, 1913, vol. lxxxii. p. 158.
 ‡ *Metallurgical and Chemical Engineering*, 1913, vol. xi., No. 3, p. 167.
 § *Ibid.*, 1913, vol. xi. (8), p. 449.
 ‖ *Metal Industry*, 1913, vol. v. p. 265.   ¶ *Ibid.*, p. 179.
 ** *Brass World*, 1913, vol. ix. p. 251.

towards a more scientific and economical treatment of scrap metal of all kinds. The following table, showing the amount of various metals recovered from scrap in the United States, will render evident the increase of business in this trade during 1912:—

Metal.	1911.		1912.	
	Short Tons.	Value, Dollars.	Short Tons.	Value, Dollars.
Secondary copper	50,845	12,711,250	66,441	21,593,325
Remelted brass	80,370	16,814,400	101,523	27,279,516
Secondary lead	27,359 }	4,882,860	30,266 }	6,045,120
Recovered in lead alloys . .	26,895 }		36,902 }	
Secondary zinc	44,714 }	5,464,800	52,251 }	7,750,494
Recovered in zinc alloys other than brass	3,223 }		3,912 }	
Secondary tin	7,749 }	12,353,040	8,333 }	14,301,368
Recovered in tin alloys . . .	6,957 }		7,068 }	
Secondary antimony . . .	10 }	359,040	13 }	426,020
Recovered in antimony alloys .	2,359 }		2,493 }	
		52,585,390		77,395,8 43

Most of the copper was obtained from scrap brass; whilst secondary lead largely obtained from bearing metals, old lead pipe, and sheet lead. Tin was largely recovered from tinplate scrap.

World's Copper Production in 1912.—The world's output of copper in 1912 amounted to 1,004,485 tons, an increase of 132,565 tons over the figure for 1911. In 1893 the total production of copper was only 303,530 tons.*

World's Metal Production during 1912.—The annual tables published by the *Metallgesellschaft* contain † the following values for the output of the chief non-ferrous metals during the year 1912.

	1912.	1911.	1910.
	Metric Tons.	Metric Tons.	Metric Tons.
Copper	1,019,800	893,400	887,900
Tin	123,100	118,700	115,790
Lead	1,189,100	1,132,900	1,128,500
Zinc	997,900	902,100	816,500
Aluminium	61,100	45,000	43,800
Nickel	28,500	24,500	20,100
Mercury	4,300	4,100	3,600

Of the above metals copper shows the largest increase in production (14 per cent.) as compared with the year 1911; whilst the output of

zinc shows an increase of $8\frac{1}{2}$ per cent., lead 5 per cent., and tin 2·7 per per cent. Production and consumption of the total output are credited to Europe and the United States are as follows :—

	Production (per Cent. of Total Output).		Consumption (per Cent. of Total Output).	
	Europe.	U.S.A.	Europe.	U.S.A.
Lead	45·6	32·5	59·4	33·5
Copper . . .	19·3	58·1	61·3	36·5
Zinc	67·6	32·2	67·4	31·9

An all round increase in the production of aluminium has taken place except in the United States. The increase in nickel output is ascribed almost entirely to Canada and the United States.

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* In the library of the Institute.

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> [A treatise claiming to cover the whole field of general metallurgy, and to give special attention to the results of modern research. The author has treated the subject from the point of view of the metallurgist who has a leaning towards physical chemistry, and has also devoted special attention to those mechanical processes so much in evidence in present-day metallurgical practice.]

HOFFMANN, F. *Atomprozente und Gewichtsprozente : Sowie die Methoden zu Ihrer Gegenseitigen Umwandlung.* 8vo, pp. 20, with 18 diagrams and 2 double (superimposed) plates. Halle : W. Knapp.

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Lord, Nathaniel Wright, and Dana J. Demorest. *Metallurgical Analysis.* Third edition. Revised, Reset, and Enlarged. 330 pages, $5\frac{1}{2} \times 8''$, illustrated. 1913. New York: McGraw Hill Book Company. (Price 10s. 6d. net.)

   [Amongst other matters there are chapters on the following: Obtaining and preparing samples for analysis; determination of spelter and tinplate coating; zinc in ores, copper in ores, lead in ores, tin in ores. Analyses of: Refined copper, refined lead, bearing metals, spelter, brass and bronze, coal and coke, clays and other silicates; softening water for boiling use.]

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   [This issue of *Metal Statistics* will be found to be an improvement over previous issues as regards completeness and extent of the statistical information contained in it. Statistics are given with regard to copper, tin, lead, iron and steel, spelter, aluminium, antimony, silver, gold, mercury, and platinum.]

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Molinié, E. P. C. *L'Argent et les Métaux de la Mine de Platine.* Pp. 400, with 93 text illustrations. Paris: O. Doin & Fils. (Price 4s. 2d.)

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   [Contains chapters on: Wiring and equipment of the laboratory, conductivity of electrolytes, electromotive force, electro-analysis, electroplating, electrolysis of molten salts, electro-furnace processes.]

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[This new edition of an invaluable work is substantially the same as the first edition. However, there have been added an essay by MM. Osmond and Cartaud on " Polishing," and " Some General Notes on the Practical Application of Metallography," by Stead.]

OSTWALD, WILHELM. *Outlines of General Chemistry.* Translated from the German edition by W. W. Taylor. Third edition. London: Macmillan & Co., Limited. (Price 17s. net.)

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[The volume is divided into three parts, followed by an appendix, containing bibliographic references. Part I. is of most interest to metallurgists; it contains descriptions of the industries and processes attended with risk of poisoning; incidence of such poisoning. (1) Chemical industry; (2) recovery and use of metals; (3) other industries.

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SOURIS, A. *Le Blanc de Zinc et le Lithopone, leurs Qualités et leurs Emplois.* Second edition, revised. 8vo. 1913. Paris: Béranger. (Price 10d.)

Tables Annuelles de Constantes et Données Numériques de Chimie, de Physique et de Technologie. Publiées sous le Patronage de l'Association internationale des Académies, par le Comité international nommé par le VIIe. Congrès de Chimie Appliquée (Londres.) Vol. ii. Année 1913. 4to, pp. 758. 1913. London: J. & A. Churchill. (Price 28s. 6d.)

Text-Book of Rand Metallurgy. Vol. I. (second edition.) 466 pages, 8 ins. × 5 ins. 128 illustrations. Vol. II.—438 pages, 455 illustrations, and 33 tables. 1913. London: Charles Griffin & Co., Limited. (Price 21s. net each.)

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WEIDIG, MAX. *Metallurgische und technologische Studien über das Ausglühen von Metallen und Legierungen.* Large quarto (22×30 centimetres), 121 pages. 48 illustrations. Berlin: Leonhard Simeon. (Price 6 marks.)

  [One half of the book reviews the results of other workers on the influence of annealing on the structure and mechanical properties of metals and alloys; the second half contains the results of experiments by the author upon copper, nickel, copper-nickel, brass, aluminium bronze, tin bronze, tin-zinc bronze, german silver, and aluminium.]

WREN, HENRY. *The Organometallic Compounds of Zinc and Magnesium.**
1913. 100 pages 8vo. Edited by A. C. Cumming, D.Sc. London: Gurney & Jackson. (Price 1s. 6d. net.)

  [This book, the first of a series of monographs, is intended, primarily, for the use of Advanced and Honours Students in Chemistry. The book should also prove useful to those engaged in research.]

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Form A.   (*Membership Application.*)

INSTITUTE OF METALS.

Founded 1908.   *Incorporated 1910.*

To the Secretary,

I, the undersigned.., being
of the required age and desirous of becoming a ....Member of
the INSTITUTE OF METALS, agree that I will be governed by the regulations
of the Association as they are now formed, or as they may be hereafter
altered, and that I will advance the interests of the Association as far as
may be in my power ; and we, the undersigned, from our personal know-
ledge, do hereby recommend him for election.

Name in full..

Address...

Business or Profession......................................

Qualifications..

....

Signature...

Dated this..............day of...................., 191 .

.... ⎫
.... ⎬ Signatures
of three
.... ⎭ Members.

The Council, having considered the above recom-

mendation, present Mr........................to be Balloted for

as a....................Member of the INSTITUTE OF METALS.

To be filled up
by the
Council.

....
CAXTON HOUSE,   *Chairman.*
    WESTMINSTER, S.W.,

Dated this.................day of.................191......

[FOR QUALIFICATIONS OF MEMBERS, SEE SECTION 1, OTHER SIDE.]

(*It would be a convenience if the Candidate's Card were sent with this form.*)
x.

EXTRACTS FROM THE RULES.

(MEMORANDUM AND ARTICLES OF ASSOCIATION.)

SECTION I.—CONSTITUTION.

Rule 4.—Members of the Association shall be either Honorary Members, Fellows, Ordinary Members, or Student Members.

Rule 5.—*Ordinary Members* shall be more than twenty-three years of age, and shall be persons occupying responsible positions.   They shall be :—
> either (a) persons engaged in the manufacture, working, or use of non-ferrous metals and alloys ;
> or (b) persons of scientific, technical, or literary attainments connected with or interested in the metal trades or with the application of non-ferrous metals and alloys.

Student Members shall be more than seventeen years of age, and shall not remain Student Members of the Association after they are twenty-five years of age, and shall be :—
> either (a) Students of Metallurgy ;
> or (b) pupils or assistants of persons qualified for ordinary membership whether such persons are actually members of the Association or not.

Student Members shall not be eligible for election on the Council nor entitled to vote at the Meetings of the Association.

SECTION II.—ELECTION OF MEMBERS.

Rule 6.—Applications for membership shall be in writing in the form marked " A," and such application must be signed by the applicant and not less than three members of the Association.

Rule 7.—Such applications for membership as Ordinary Members or Student Members as are approved by the Council shall be inserted in voting lists.   These voting lists will constitute the ballot papers, and will specify the name, occupation, address, and proposers of each candidate. They shall be forwarded to the members for return to the Secretary at a fixed date, and four-fifths of the votes recorded shall be necessary for the election of any person.

Every such election shall be subject to the payment by the applicant of his entrance fee and first annual subscription, and he shall not become a member of the Association nor be entered on the Register of Members until such sums are actually received from him.   In the event of his failing to pay such sums within the time specified in the notification to him of his election, his election shall be void.

Rule 8.—Upon election under the preceding Article the Secretary shall forward to the applicant so elected notice thereof in writing in the form marked " B."

Rule 9.—In the case of non-election, no mention thereof shall be made in the minutes.

SECTION VI.—SUBSCRIPTIONS.

Rule 28.—The subscription of each Ordinary Member shall be two guineas per annum, and of each Student Member one guinea per annum.   Ordinary Members shall pay an entrance fee of two guineas each, and Students an entrance fee of one guinea each.

Rule 29.—Subscriptions shall be payable in advance on July 1st in each year, save in the case of Ordinary Members and Student Members elected under Clauses 6 and 7 hereof, whose entrance fee and annual subscription shall become payable in accordance with the notification to them of their election.   Every subscription shall cover the period down to the 30th of June next following, and no longer.

Rule 30.—Subject to the provisions of Clause 7 hereof, any member whose subscription shall be six months in arrear, shall forfeit temporarily all the privileges of the Association.   Due notice on the form following marked " C " shall be given to such member, and if such subscription remains unpaid upon the date specified for payment in this notice, the Council may remove such member from the Register of Members of the Association, and thereupon any member whose name is so removed shall cease to be a member thereof, but shall nevertheless remain liable to the Association for such arrears.

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